

TWENTY YEARS' PROGRESS IN EXPLOSIVES.^a

[With 9 plates.]

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I.

From the time of the invention of gunpowder, or approximately in the year 1250 (Roger Bacon at any rate knew of it in 1264), until the beginning of the nineteenth century no other explosive was introduced into practice, although picric acid and fulminate of mercury were known about the latter date. Experiments were carried out by Le Blond in 1756 in the French Government factory at Essonne to produce gunpowder without sulphur, and a British patent for a powder containing "coal brasses" and without charcoal was taken out by Delaval in 1766,^b but that was all. In 1788 Berthollet and Lavoisier tried the effect of adding potassium chlorate, and in 1861 Designolle made a powder from potassium picrate and saltpeter, but without much success. In 1846 Schoenbein invented gun cotton, and Sobrero in 1847 nitroglycerin, but the Austrian Government, which was the only one to try gun cotton in guns, stopped the experiments abruptly in 1867, their magazines at Hirtenberg having blown up, and, curiously enough, it is not until that date that Nobel began to work on dynamite. About the same time the British Government began to experiment with gun cotton at the point where the Austrians had left off, and introduced it as a blasting agent into the service, their example being then followed by other governments. In 1873 Sprengel made his well-known communication to the chemical society "on a new class of explosives," which has since been named after him; and in 1878 it was again Nobel who invented blasting gelatine. About 1864 Abel and Doctor Kellner, of Woolwich Arsenal, made a granular gunpowder from gun cotton, and at the same time a sporting powder

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^b Thomas Delaval, British patent No. 846, of 1766.

from nitrated wood, the Schultze powder, was introduced. Later on, in 1882, Reid made grains of soluble gun cotton, and hardened them by means of ether alcohol, calling the product "E. C. powder." In the third lecture reference will be made to the important smokeless powder of Friedrich Volkmann made in 1870.

Such was the state of the art in 1886, when simultaneously Eugène Turpin, of Paris, suggested the use of compressed or molten picric acid as a charge for shells, and Vieille carried out his famous experiments, resulting in the manufacture of the Poudre B (so named after General Boulanger). At the same time it was recognized that most explosions in coal mines were due to the ignition of fire-damp by the firing of shots, and that it was possible to make so-called "safety explosives," which would considerably reduce this danger.

Hereafter investigations and inventions came in almost too rapid succession. Unfreezable dynamites, dinitroglycerin explosives, picric acid compounds and trinitrotoluene explosives, fulminates from aromatic nitro-compounds, phlegmatized fulminate, detonating fuses, and many other varieties were invented. Nitrocellulose, than which there is hardly a more complex substance, was investigated by Cross and Bevan, Häusermann, Lunge, de Mosenthal, Vignon, Will, and others; the stability of nitro-compounds, the properties of nitroglycerin, and many other substances investigated by an army of workers. In fact, quite as important results have been obtained since 1886 as in the whole of the previous years. This is due, in the first instance, to the enormous amount of scientific research and experiment devoted by manufacturers to the study of such questions, partly because they were forced to do so by considerations of national defense, the advent of the rock drill, and by competition, and partly because those who lacked the training for such research could be persuaded by the results achieved to appreciate the work of others. Whilst until a generation ago the so-called "powder maker" was a craftsman, who carefully guarded little *tours-de-main* as valuable trade secrets, and even the inventors of high explosives had to advance in a most empirical way, it is recognized nowadays that only the best scientific knowledge can effect improvements or keep in line with modern developments of the industry.

Whilst for warlike purposes the use of black powder, and even that of the later brown powder, has become a negligible quantity, blasting powder is still sold to such an extent that in the mines and quarries of this country alone nearly 7,000 tons of it, or more than half the total weight of all explosives, were used in 1907.^a This of course represents only part of the total quantity manufactured in this country, since 3,597 tons of gunpowder of all kinds of British and Irish

^a Report of His Majesty's inspectors of explosives for 1907.

production were exported,^a and a good deal was used for railways, roads, etc.

There has been practically no progress made in black powder within the last twenty years. Brown powder, which, as is known, contained slack burnt charcoal and a small percentage of sulphur, greatly improved the shooting of large guns, but has gradually given way to smokeless powder, even for the very largest guns. A little black powder is still used as a primer for large charges, but even for that purpose it will gradually be replaced by specially prepared smokeless powder. There are still some old sportsmen who prefer to use nothing but the old fine black sporting powder, and this is more especially the case in remote parts of Germany, Austria, and Italy, whilst in the United States of America professional sportsmen, i. e., those who shoot wild fowl for the market, use black powder because of its cheapness. There is a certain amount of competition going on in this quarter with smokeless powder, and manufacturers of black sporting powder are thereby obliged to make special efforts to produce material of the highest grade only.

The enormous development of the German potash industry, and the peculiar requirements of potash and salt mining, have also revived some rough mixtures of black-powder-like explosives, of which very large quantities are now sold in Germany.

In America, also, large quantities of black powder made with sodium nitrate are used. Labor there is so expensive that work is done with this cheap explosive which on this side of the Atlantic would be carried out with pick and shovel.

Progress of a different kind has been effected by using ammonium nitrate as an ingredient in a powder mixture. This also was tried in France in the eighteenth century with but little result.^b Amide powder,^c however, made by the Koeln-Rottweil works, and consisting of 40 parts of potassium nitrate, 38 parts of ammonium nitrate, and 22 parts of charcoal, might, but for the advent of smokeless powder, have become a serious rival to black powder. Mayer, of Felixdorf, in Austria, also worked in this direction. The Austrian Government makes Wetter-Dynammon as an explosive for fiery mines, which, according to Ulzer,^d consists of 93.83 per cent of ammonium nitrate, 1.98 per cent potassium nitrate, 3.77 per cent charcoal, and 0.42 per cent moisture, the charcoal grains being 1 to 6 μ in size.

^a Private communication.

^b Bottée et Riffault, "Traité de l'art de fabriquer la poudre à canon." Paris, 1811.

^c Gaens, British patent No. 14412, of 1885.

^d "Mitteilungen des technologischen Gewerbemuseums," Wein, 1900, p. 204.

Further progress, although seemingly small, has been that made in powder for safety fuses. Formerly it was not uncommon to use the siftings from mining powder for safety fuses, but the present stringent requirements have compelled all manufacturers to make a special quality of fuse powder of constant composition, density, and uniformity of granulation, in spite of its almost dustlike character.

I shall lay before you later on some information concerning safety explosives for fiery mines, and, therefore, will only mention that in every European country the use of gunpowder is prohibited in such workings. Considerable surprise was therefore felt when several black-powder-like mixtures passed the official test for permitted explosives in this country. Later, when these tests were made more rigorous, these explosives disappeared, but one of them, bobbinite, passed even the more stringent tests, and is still on the new list of permitted explosives.

Complaints having been made as to the alleged danger of bobbinite in fiery mines, the home office appointed a departmental committee in 1906 to investigate the matter, which came to the conclusion that the use of bobbinite should not for the present be restricted.^a The importance of this explosive may be gauged from the fact that over a million pounds of bobbinite were used in 1907 in this country.

With regard to machinery used in the manufacture of black powder and similar mixtures there has, of course, been very little improvement. Mixing, granulating, and glazing are still carried out in the same way, and for the purpose which they have to accomplish the machines do all that can be desired. A good deal of ebonite was formerly used in connection with machinery for black powder, such as for plates in cake presses, for lining the hoppers of cutting machines, etc. In cake presses there are alternate layers of powder containing sulphur, and of highly insulating ebonite, which remain together under pressure for some time. It is a rule in explosives works that at the approach of a thunderstorm the workers leave their houses, and it is frequently found convenient, meanwhile, to leave the charge under pressure. This would practically constitute an electric pile, and as a matter of fact several explosions have occurred when, after the thunderstorm, the workers opened the presses. In one instance, at least, the fact of a long spark having come out of the charge could be elicited from the attendant before his death.

Following a suggestion made by the author twenty years ago, a number of factories have substituted plates of fiber for these ebonite plates with great success.

^a Report of the Departmental Committee on Bobbinite. London, 1907.

Chlorate mixtures have at all times fascinated inventors on account of the large amount of oxygen stored up in potassium chlorate, which can be given off so readily. When Lavoisier and Berthollet tried to make a chlorate powder in a stamp mill in 1788, they made a great show of it, and even two ladies were present. Unfortunately after a certain amount of pounding the powder exploded and killed an official and the daughter of the government commissary, who assisted at the experiments.

In this country we have for a long time refrained from licensing any explosive containing potassium chlorate, because such are so easily exploded by impact or friction. With the advent of electrolytic methods for the manufacture of chlorine, potassium chlorate, and the like, chlorate explosives were brought within easy reach of the trade, and in fact the present price of electrolytic potassium chlorate will under certain conditions permit the economical manufacture of suitable explosives. Hence greater efforts were made to render chlorate explosives more stable, so as to pass the home office test, and ultimately success was attained by the addition of some oil. Its function is evidently to so surround the potassium chlorate that, when mixed with carbonaceous matter, it becomes less sensitive. The addition of greasy matter to chlorate explosives is not at all a new idea. In 1867 already F. Hahn added spermaceti to a gunpowder containing chlorate.^a However, a practical explosive was ultimately obtained in cheddite, patented by Mr. Street,^b and so called because it was first made in Chedd, in Switzerland. The more usual variety is known abroad under the name of cheddite 60 bis, and its composition is 80 parts of potassium chlorate, 13 parts of mononitronaphthalene, 2 parts of dinitrotoluene and 5 parts of castor oil, whilst in this country the proportions of mononitronaphthalene and dinitrotoluene are reversed.

It is interesting to observe how the same old mixtures are proposed over and over again with slight alterations only, in order to qualify for a patent. Potassium chlorate with some carbonaceous matter like charcoal, sugar, starch, glycerin, flour, or sometimes a vegetable or mineral oil and the like occurs again and again. One patent^c is of special historical interest, since it proposes the use of "Maltha" as an ingredient. The patentees came from California, an English-speaking country, and therefore it might be supposed that the name was not unfamiliar in England, but this appears not to be the case. I recollected, however, a passage in Roger Bacon's "Opus Majus" as follows: "Nam Malta, quæ est genus bituminis et est in magna copia in hoc mundo, proiecta super hominem armatum comburit

^a British patent No. 960, of 1867.

^b Id., No. 9970, of 1897.

^c Quinby, Sharps and Greger, British patent No. 4781, of 1902.

eum"—(Thus Malta, which is a kind of bitumen, and exists in large quantities in this world, when thrown on an armor-clad man, burns him to death). It seems, therefore, that the *Mayflower* took with her some Old World expressions and adapted them to the New World.

The latest surprise is that in 1908 a chlorate explosive has been licensed as a safety explosive in this country under the name of "colliery steelite;" it consists of 74 parts of potassium chlorate, 25 parts of oxidized resin, and 1 part of castor oil.

The electrolytic chlorine industry has also made possible the manufacture of pure perchlorates, and more especially of ammonium perchlorate, which presents many advantages, although the objection has been raised that explosives containing this ingredient generate fumes of hydrochloric acid in the mine.

Another class of explosives, which was from time to time used for ordinary blasting purposes, and of which very little has been heard in this country, are the Sprengel explosives. You have all heard of rackarock, which was employed in the blasting of the Hell Gate rocks near New York. Until the last decade it was hardly used anywhere except in America, but on building the first Chinese railways the Americans were able to introduce it.^a

A novel ingredient was introduced by Winand,^b who mixes tetranitromethane with petroleum or other carbonaceous matter.

A new departure was made in 1899, when Dr. Richard Escales, of Munich, invented the first aluminum explosive. There were only a few early attempts to utilize light metals in explosives, until Escales showed that the addition of aluminum or magnesium very considerably increased the temperature of explosion and thereby the explosive force. His explosive was patented under the name of Wenghoeffler,^c and is now, I believe, manufactured, together with a similar explosive invented independently in 1900 by Ritter von Dahmen,^d and since known under the name of "ammonal."

Ever since aluminum has been taken as an ingredient in almost any kind of explosive. Theoretically it would be of very great value, but in practice the high price of aluminum powder and the possibility of oxidation under suitable conditions have somewhat militated against it. It is, however, used in Austria-Hungary for filling shells, for which purpose it seems well suited, not having given any trouble during ten years of storage, although I am told they sometimes fail to explode. It is also on the special list of the British home office as an explosive for fiery mines.

^a Károly Gubányi, "The Rackarock Blasting Powder," "Magyar mérnök és építész egyesület közlönye," 1901, p. 165.

^b British patent No. 26261, of 1907.

^c British patent No. 24377, of 1899.

^d Id., No. 16277, of 1900.

Other metals might have a similar or even a better effect than aluminum. Thus in 1900 already Désiré Korda, of Paris, and the author have considered the possibility of using ferro-silicon. In addition to the above-mentioned metals, the use of iron, silicon, silicon carbide, zinc and its alloys, copper, and also the rare metals has been patented.

In his patent of 1871 on the explosives bearing his name,^a Prof. Hermann Sprengel, F. R. S., said, seemingly without reference to the rest of the patent, "I also employ picric acid," but in his famous lecture delivered in 1873 before the Chemical Society he said distinctly: "Be it noticed here that picric acid alone contains a sufficient amount of available oxygen to render it, without the help of foreign oxidizers, a powerful explosive, when fired by a detonator. Its explosion is almost unaccompanied by smoke." As a matter of fact, Sprengel did fire some shots with picric acid at Messrs. John Hall & Sons' factory in Faversham in 1871, but was not encouraged by the service to pursue his experiments.

Nothing further was heard of picric acid until 1886, when, as mentioned before, Eugène Turpin, of Paris, showed how to compress or melt it for use in shells. The French service used picric acid, mixed with collodion to give it greater density, under the name of melinite. Later on it was compressed, but ordinary detonators failed to explode it with safety, and the expedient devised by Alberts and the author to use a primer of dry gun cotton was too inconvenient. The picric acid has therefore to be melted, in which state it can be more readily exploded by detonators, and has a density of about 1.65. Picric acid melts at 122.5° C., and must therefore be either heated in an oil bath by high-pressure steam or in a special "stove." Melting it at such a high temperature is very inconvenient and is not without danger, hence use was made of the well-known phenomenon that a mixture of two substances of high melting points has nearly always a lower melting point than that of either of its constituents. Girard^b has given a long list of the melting points of explosive mixtures of this kind.

Almost every country has adopted picric acid as a disruptive agent, under a different name, and differences in composition consist merely in the addition of an ingredient to reduce the melting point. Such additions are nitronaphthalene, camphor, dinitrotoluene, etc., and the names are melinite, lyddite, pertite, shimose powder, picrinit, ecrasit, etc.

Besides having a high melting point, picric acid is inconvenient in other ways. Left in contact with metals or oxides it forms very dangerous picrates, hence the necessity of varnishing the interior of

^a British patent No. 2642, of 1871.

^b Id., No. 6045, of 1905.

shells, giving special protection to the primers, and generally taking the utmost precaution to prevent access of foreign bodies while the acid is in the molten state. Picric acid has an intensely bitter taste (which is still more pronounced in the inky black smoke of burning picric acid), and therefore its manipulation is not very pleasant. It also imparts a fairly fast yellow coloration to the skin, which in some parts has procured the nickname of "canary birds" to the workers in picric acid. (I have found that in one factory common salt was used for removing the yellow coloration from the skin, but why it should do so is not quite clear.) When used together with other materials it must be remembered that, being an acid, it is liable to displace other acids; for instance, it sets free nitric acid from nitrates, and therefore while picric acid might be useful for increasing the power of certain explosives it would actually decompose them.

In order to obviate these drawbacks Hauff had proposed the use of trinitroresorcine^a and the Chemische Fabrik Griesheim that of trinitrobenzine^b and trinitrobenzoic acid.^c These substances were not favorably received, but trinitrotoluene has within the last few years come very much to the fore, and also possesses a great many good qualities. Its melting point varies between 72° and 82° C. It may be handled with almost perfect safety if pure, does not give off noxious fumes on melting, is quite stable, does not combine with metals, and generally has no acid properties. Like picric acid it is only slightly soluble in cold water. It is slightly less powerful than picric acid, which is rather an advantage, since the latter frequently pulverises a shell, instead of bursting it into a number of fragments sufficiently large to have destructive effect. Trinitrotoluene is very easily detonated. I have been able to explode it in the form of powder, with a No. 3 detonator only (0.540 gram of fulminate composition).

Trinitrotoluene has been introduced into the French service under the name of tolite. The Spanish Government call it trilit. The carbonite works of Schlebusch are introducing it into other services under the name of trotyl, and Messrs. A. and W. Allendorf, of Schönebeck, under the name of trinol, whilst other factories retain the name of trinitrotoluol.

The manufacture of trinitrotoluene is carried out in stages, like that of most aromatic nitro compounds. Great care has to be taken to purify the toluene, since that usually found in commerce contains benzene and other compounds. Nitration is effected in enameled iron vessels, and purification of the higher nitrates, which cake together during nitration, has to be performed with some care. Wash-

^a British patent No. 9798, of 1894.

^b German patent No. 79477, of 1893.

^c Id., No. 79314, of 1893.

ing is usually completed in centrifugals. In order to obtain the best quality, melting between 81° and 82° C., trinitrotoluene made from purified toluene, and having a melting point of 77° to 79° C., is recrystallized from alcohol in vacuo. The machinery for effecting this is not very complicated, but always specially designed. In this country alcohol is somewhat dear and inconvenient to use, in spite of facilities afforded for obtaining it duty free, and petroleum benzine is therefore employed for recrystallizing the trinitrotoluene; it is said, however, that a slightly darker color is imparted by this method to the product, to which objection is taken in some countries.

The density of trinitrotoluene when loose being 1.50 and when molten 1.600, means have been devised to increase it. Rudeloff^a obtains a density of 1.85 to 1.90 by making a plastic substance from trinitrotoluene and potassium chlorate with a gelatine made from dinitrotoluene and soluble nitrocellulose. Bichel makes a plastic compound with collodion cotton, liquid dinitrotoluene, and larch turpentine, calling it plastrotyl.^b Messrs. Allendorff mix the trinitrotoluene, together with some lead nitrate or chlorate, with a gelatine made from dinitrotoluene and nitrocellulose, and call it triplastit. This is an improvement on the way the French Government made melinite with collodion, or Wolff & Co. filled gun-cotton slabs into shells with paraffin wax. Bichel also melts the trinitrotoluene, and after first exhausting all occluded air, compresses it by introducing compressed air above it.^c Bichel has in this way obtained densities up to 1.69. Rudeloff presses it in hydraulic presses under a pressure of 2,000 to 3,000 atmospheres, whereby it obtains a density of 1.7, and can be cut and worked like gun cotton. For the purpose of facilitating detonation, some loose trinitrotoluene is used as a primer. Trinitrotoluene is also used in detonators, of which further mention will be made later on.

Another new explosive for filling shells is used in Spain under the name of tetralit.^d It is said to be made from tetranitromethylamine, and to be more sensitive than trinitrotoluene, but very little else is known.

During the last three or four years newspapers contained accounts of trials with a new explosive, at first called vigorite and now bavarite, the invention of Professor Schulz and Mr. Gehre, which is said to cost only one-third as much as other explosives, and to be ever so much more powerful. On examining the patent^e one finds that this

^a "Zeitschrift für das gesamte Schiess- und Sprengstoffwesen," 1907, p. 7.

^b British patent No. 16882, of 1906.

^c Id., No. 19215, of 1906.

^d "Zeitschrift für das gesamte Schiess- und Sprengstoffwesen," 1908, p. 308.

^e British patent No. 5687, of 1905.

is nitrated solvent naphtha. It must be embarrassing to the inventors to see such improbable accounts of manufacturing costs and exaggerated effects produced by the explosive published in newspapers.

II.

I have mentioned in my previous lecture that Sobrero invented nitroglycerin in 1847. It is known that, although he recognized the value of this invention for civil and military blasting purposes, practically no use was made of it until 1867, when Alfred Nobel invented dynamite, and was not deterred by accidents and prejudice from introducing it into the service of mankind. You know that before this time Mowbray, in Massachusetts, manufactured nitroglycerin and carried it into the mines in the frozen state.

Nobel devised processes for the manufacture of nitroglycerin on a large scale, and the machinery for it was constructed to his ideas by his lifelong adjutant, Mr. Alarik Liedbeck, of Stockholm. Since there is a full description of all the apparatus in use in my book on *The Manufacture of Explosives*, which appeared in 1895, I can confine myself to dealing with progress made since that date. You will find described in this book two kinds of apparatus for nitrating glycerin, such that have a helical revolving stirrer for mixing purposes and such that are agitated by compressed air. Occasionally both mechanical and compressed air stirring are used. One has learned in time to control the operation of nitration more efficiently, and this inspired confidence to increase the size of the apparatus. I believe the largest apparatus made in lead nitrates 680 kilograms of glycerin at one operation, while in America and South Africa steel apparatus with mechanical stirring gear are mostly used, some nitrating 1,000 kilograms at a time. In one United States works they have gone so far as to have four such steel nitrators, each for a charge of 1,000 pounds of glycerin, in one room and driven from one main shaft, but present practice is to have two such nitrators in one building. In this country one would not allow more than one nitrating apparatus to be used at a time. Of course each nitrator is provided with a series of lead or steel coils through which cold water circulates, and it has now become frequent to install a refrigerating plant and to circulate water of only 10° C. and less through the coils.

With regard to the composition of the nitrating mixture, it has been customary in well-conducted factories during the last twenty years or so to nitrate 110 kilograms of glycerin in a mixture of 300 kilograms of nitric acid of about 93 to 94 per cent monohydrate and 500 kilograms of sulphuric acid of 96 per cent monohydrate (and not, as Sir Frederic Nathan and Mr. Rintoul stated, 100 parts of glycerin

and nitric acid of 91 per cent only).^a This corresponds to about 255 parts of nitric acid monohydrate and 436.4 parts of sulphuric acid monohydrate, or a total of 691.4 parts of acid monohydrate with 35.8 parts of H_2O (4.9 per cent) to each 100 parts of glycerin.

It is now customary to add sulphuric acid containing 20 per cent of anhydride (oleum) to the original mixture, but it is still found impracticable to add it to the waste acid. It will be seen from the paper of Sir Frederic Nathan and Mr. Rintoul on "Nitroglycerin and its manufacture" that the use of anhydride has reduced the quantity of sulphuric acid required. Five years ago already I found in the Pozsony factory of Nobel's the use of mixed acid consisting of 37.2 per cent HNO_3 , 60 per cent H_2SO_4 , and 2.8 per cent H_2O , and made with anhydride. Although no artificial refrigeration was used, the yield of nitroglycerin amounted to 220 for 100 glycerin, and a ratio 6.318 of acid to 1 of glycerin. Factories using Nathan, Thomson, and Rintoul's process now employ a mixture of 41 per cent HNO_3 , 57.5 per cent H_2SO_4 , and 1.5 per cent H_2O , corresponding to 250 pounds HNO_3 , 350 pounds H_2SO_4 , and 9 pounds H_2O for each 100 pounds of glycerin, which gives a ratio of 6.09 of acid to 1 of glycerin, as against 6.91 to 1 formerly required. It is thus seen that this process requires about the same quantity of nitric acid per 100 glycerin as the old process, but about 86 pounds, or roughly 20 per cent, less sulphuric acid. It will therefore simply depend upon the price of the sulphuric anhydride whether it is advantageous to use it.

With the present prices of £3 per ton of 96 per cent sulphuric acid and £3 15s. 0d. per ton of sulphuric monohydrate, containing 20 per cent of anhydride, the difference between the cost of materials with the former yield of 220 and the present one of 229 nitroglycerin is, per ton, £3 0s. 2d, or approximately 5.6 per cent.

This apparent saving is quite counterbalanced by the fact that in the new process 1.9 tons less of waste acid are obtained.

In making this comparison it must, however, be remembered that with the new process the same apparatus will hold 18 per cent larger charges.

After nitration the mixture is allowed to stand, when the nitroglycerin separates from the waste acid and floats on the top of it. The separation is sometimes considerably delayed by the formation of a silicious colloid, which agglomerates with particles of cell substance and other impurities, forming fern-like growths. The Dynamit Actiengesellschaft in Hamburg^b found a very efficient means of promoting separation in the addition of high-boiling paraffins in

^a Journal of the Society of Chemical Industry, March 16, 1908. Compare also Guttman. Manufacture of Explosives, Vol. II, p. 93.

^b British patent No. 13562, of 1904.

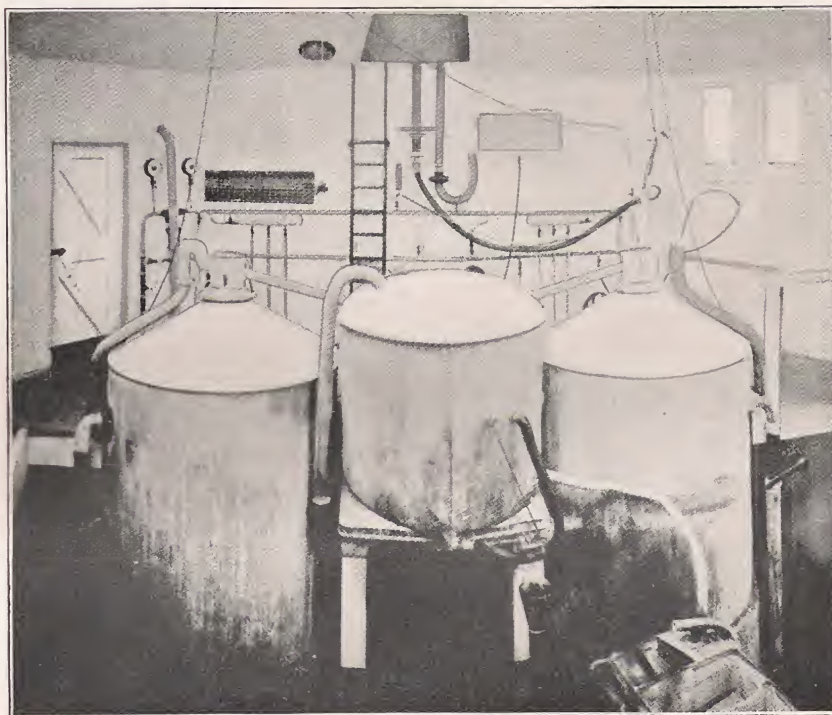
quantities of 0.5 to 2 per cent of the weight of glycerin, while Dr. L. F. Reese, of Wilmington,^a adds as little sodium fluoride as 0.002 per cent (1 in 50,000) of the glycerin employed to the nitrating mixture with excellent results. Both methods are now used in very large factories. For more than thirty years some factories had been in the habit of employing one vessel only for both nitrating and separating, and withdrew the nitroglycerin from three earthenware cocks, placed at short intervals at the separating line. This enabled them to gain considerably in levels and to carry out the manufacture right up to the final washing on practically the same level.

The waste acid was always sent to after-separation houses, which were frequently called by the German name of "Nachscheidung." Since the waste acid sometimes had to be kept in these after-separation houses for a week, in order to get rid of all the drops of nitroglycerin which separated out, decomposition occasionally set in. A plan was thereupon introduced in France and elsewhere which consisted in gradually diluting the waste acid by the addition of from 2 to 3 per cent of water, thereby stopping the further formation and separation of nitroglycerin.

At the government factory at Waltham Abbey these methods have been improved upon. A so-called "nitrator separator" is used, in which the nitroglycerin has time to separate from the acids, and waste acid is then added from below, thereby bringing the level of the nitroglycerin to a point where it will run out through a gutter into the preliminary washing tank. In this way the use of cocks is avoided. When all the nitroglycerin has been displaced about 2 per cent of water is introduced gradually.

The result of this combination of a number of useful processes, namely, the employment of anhydrous sulphuric acid to produce a mixed acid containing little water, the use of refrigerated water to cool the acids, the displacement of the nitroglycerin by means of waste acid, which obviated the remixing of acid and nitroglycerin on emptying the nitrator, and the addition of water to stop the separation of further quantities of nitroglycerin, was that they together contributed to yield much better results. As a matter of fact in well-conducted works the yield of nitroglycerin with the proportions of 6.91 to 1 mentioned above was between 217 and 220; at Waltham Abbey it was possible to obtain by the "displacement process" a yield of 229 parts nitroglycerin for 100 parts glycerin, instead of the former 220 parts. According to Mr. de Mosenthal the Nobel works obtained similar good results. This yield has to the author's knowledge been only once exceeded in a Belgian factory, when a charge of nitroglycerin had to be drowned on a cold winter's

^a British patent No. 20310, of 1905.



NITRATOR SEPARATOR (NATHAN, THOMSON, AND RINTOUL'S PATENT).



CALCINED KIESELGUHR.

day. The contents of the tank froze and required two days to thaw; a yield of 240 parts nitroglycerin was, however, the surprising result.

With regard to the selection of apparatus, round lead or steel tanks, as explained above, are generally used, but the author has also seen square-cornered ones. The Americans are much in favor of mechanical stirring, whilst in Europe air stirring is preferred. Having worked with both, I can not see much difference as regards results, but since I do not like to have any moving parts in connection with the manufacture of nitroglycerin I think air stirring is preferable, on the whole.

There has been no special improvement in the manufacture of dynamite since Nobel in 1875 invented blasting gelatin.

In this connection it will be interesting to have a true picture of kieselguhr as used for dynamite. Mr. Henry de Mosenthal, whose skill in preparing specimens for the microscope we had often occasion to admire, has prepared for me various slides of kieselguhr.

For blasting gelatin, as you know, a so-called "collodion cotton" or soluble nitrocellulose is employed. Many people think that if 7 per cent of nitrocellulose is insufficient to make a stiff and suitable blasting gelatin, the addition of another 1 or 2 per cent would do it, and certainly at first the resulting gelatin is so stiff and hard as to require special effort in the cartridge machines. After a few months of storage, however, or after passing over the equator into Australia, nitroglycerin is found to exude. A good nitrocellulose will give a perfectly stiff blasting gelatin, with between 6 and 7 per cent of nitrocotton, and if a $2\frac{1}{2}$ per cent solution is made in a porcelain basin, the resulting gelatine should be easily detachable after cooling, showing no signs of exudation.

There has been within recent years a revival of old ideas, but with better success, for the purpose of obviating one of the chief objections to dynamite, namely, that of freezing. It was in 1866, in Sweden, that A. E. Rudberg patented the addition of nitrobenzine to nitroglycerin for the purpose of making it unfreezable.^a The Société des Poudres et Dynamites, of Arendonck, found later^b that the addition of dinitrotoluene dissolved in nitroglycerin was very useful in lowering the freezing point. A new departure was really made when Dr. Anton Mikolajczak in 1904 patented the addition of dinitroglycerin to trinitroglycerin explosives, and at the same time indicated a practical method of manufacturing it.^c It is now made on a large scale in a factory at Castrop, in Germany. In order to understand the question better it is necessary to point to a most interesting work

^a Swedish patent, April 30, 1866.

^b British patent, No. 14827, of 1903.

^c Id., No. 8041, of 1904.

by Sigurd Nauckhoff,^a showing why nitroglycerin can sometimes be subjected to intense cooling without freezing (supercooling), and to a paper by Dr. H. Kast,^b showing that there are two kinds of nitroglycerin (one being an allotropic modification), with two different melting points, one nitroglycerin solidifying at about 13.2° and the other at about 2.1°, the melting points being 13.5° and 2.5°, respectively.

Professor Will found that dinitroglycerin is not a sure guaranty against solidification, and that under certain conditions explosives prepared with it may become solid at a higher temperature than trinitroglycerin explosives.

Of all these additions none has so far been definitely adopted for the manufacture of unfreezable dynamites, but, I believe that lately dinitrodichlorhydrine has been used with considerable success by the German works of the Nobel companies.

We now come to gun cotton. The really important step in the manufacture of gun cotton was taken when the British Government adopted a process of pulping and purifying the gun cotton, first patented by John Tonkin, jr., of Poole, near Copperhouse, in Cornwall,^c and again in combination with the compression of the pulped gun cotton, three years later, by Sir Frederick Abel.^d The next step was made when the principle of the detonation of nitrocompounds by means of a small fulminate of mercury charge, invented by Alfred Nobel,^e was extended by Mr. Brown, Sir Frederick Abel's assistant, to gun cotton.^f

Baron von Lenck, the Austrian general, who worked most assiduously as the pioneer of Schönbein's invention, used gun cotton in hanks; the British Government introduced the use of cotton waste from spinning and other operations where threads are made. The reason for this change is not quite apparent, unless it was felt that since the cotton had to be pulped in any case the cheaper waste might do just as well as the long threads. This use of cotton waste has continued ever since.

It is very curious that in the purchase and use of nitric and sulphuric acid for the nitration of gun cotton most stringent conditions are laid down with regard to freedom from mineral matter, chlorine, sulphates, arsenic, etc. Yet, as far as I could ascertain, no special precautions seem to be taken in the case of cotton to guard against

^a "Zeitschrift für angewandte Chemie," 1905, p. 11.

^b "Zeitschrift f. d. ges. Schiess u. Sprengstoffwesen," 1906, p. 225.

^c British patent, No. 320, of 1862.

^d Id., No. 1102, of 1865.

^e Id., No. 1345, of 1867.

^f Id., No. 3115, of 1868.

impurities. As a matter of fact, uncarded cotton waste as used for gun cotton generally contains a quantity of strings, wicks, colored threads, india rubber, or elastic cords, and similar leavings, showing the origin of the waste, and no amount of hand picking can free the cotton absolutely from such impurities. I have further found in cotton supplied by manufacturers of the best repute a large amount of chlorine, sulphate of lime, and sulphides, besides organic and mineral dust, which gives the cotton quite a gray appearance.

Is it not also strange that it never occurred to anybody—at least as far as I know—to ascertain whether the impurities in the cotton, brought about by forcible treatment with bleaching agents and acids, are responsible for a great deal of the instability of certain finished gun cotton and smokeless powders? I am convinced that this is the case.

Nobody seems to have given it a thought that such a complex compound as cellulose in the shape of cotton must vary to an enormous extent, both in its physical and its chemical structure, and thereby also the nitrocellulose made from it.

Let us examine the possible changes. In the first instance we have the cotton itself, which may be in any stage of ripeness.

The investigations of Leo Vignon^a on the formation of oxycelluloses and hydrocelluloses, and the behavior of their nitro compounds, show plainly how cotton and cotton waste may, by the nature of the treatment they undergo, be partly transformed into oxycellulose, which gives an unstable nitro compound, and into hydrocellulose, which has a different rate of nitration than ordinary cellulose.

I have repeatedly stated on previous occasions that in my opinion the process of nitration with a mixture of sulphuric and nitric acids results, in the first instance, in an attack on the cotton by the sulphuric acid similar to that in the manufacture of vegetable parchment, and that the sulphuric acid is gradually displaced by the nitric acid penetrating the fiber.

It seems a fact that the more oxycellulose is formed in the cotton before nitration, the more unstable are the compounds formed in the nitrocellulose. Other impurities in the cotton are all the more likely to endanger the stability of nitrocellulose, as their nature is always unknown, and varies from sweepings to india-rubber elastics, while almost all are sure to produce unstable compounds.

How far the nature and origin of the acids may have an influence upon the ultimate product has still to be investigated.

I do not think that differences in apparatus used for the manufacture of nitro-cellulose have much to do with its stability. I have strong reasons for not recommending iron vessels for stabilization in

^a Comptes rendus, June 6, 1898, September 10 and 17, 1900.

the first instance. I believe that if one must use nitrocellulose, and if, as seems to be the case, cotton is the best material for making it, one ought to use the natural cotton only, and not common yarn, and less still waste, which have both undergone so much forcible mechanical and chemical treatment as to completely alter the character of the cellulose and introduce elements of uncertainty and danger. These should be avoided by the use of ripe raw cotton, which, of course, would have to undergo suitable treatment to eliminate fat, husks, and other impurities, but would not necessitate the whole bleaching operation with its attending defects.

Formerly the mixture for gun cotton consisted of 1 part of 1.500 nitric acid and 3 parts of 1.840 sulphuric acid, and each charge was revived by taking away one-quarter of the waste acid and adding a mixture rich in nitric acid, so as to obtain about the original composition. The following table shows the result of revivifying the waste acid ten times in a series of operations made in 1886 by Doctor Abelli and the author:

Number.	Composition of nitrating mixture (proportion 1:40).			Temperature of nitration.	Yield.	N.	Soluble.	Composition of waste acid.		
	H ₂ SO ₄ .	HNO ₃ .	H ₂ O.					H ₂ SO ₄ .	HNO ₃ .	H ₂ O.
				<i>Degrees.</i>	<i>Per ct.</i>	<i>Per ct.</i>	<i>Per ct.</i>			
1.....	72.82	24.37	2.81	20	146.25	13.32	3.60	75.15	19.00	5.85
2.....	71.82	23.00	5.18	10	167.50	13.34	2.10	76.00	18.40	5.60
3.....	72.45	22.52	5.03	14	169.00	13.39	7.20	73.40	19.10	7.73
4.....	70.21	23.05	6.74	10	165.75	13.49	2.93	71.40	20.22	8.38
5.....	68.77	25.97	7.26	12	175.00	13.38	2.88	71.06	20.51	8.43
6.....	69.47	23.40	7.32	10	166.25	13.08	2.26	71.72	19.43	8.85
7.....	70.00	22.34	7.66	10	165.00	13.40	4.00	71.71	18.82	9.47
8.....	70.00	21.85	8.85	9	152.50	13.30	4.80	70.70	19.35	9.95
9.....	69.18	22.58	8.24	6	167.50	13.22	1.60	71.00	19.13	9.87
10.....	69.40	22.00	8.60	9	152.50	13.21	3.46	70.00	19.00	11.00

The original mixture consisted of 1 part of nitric acid to 3 parts of sulphuric acid, both of over 97 per cent monohydrate. Three parts of waste acid were revived with 1 part of fresh acids.

It will be seen that the percentage of nitrogen contained in the nitrocellulose reaches a maximum when the percentage of water in the acid mixture is about 9 per cent, and not, as might be supposed, in the stronger acid.

The majority of factories prepare the nitrating mixture by giving special consideration to the percentage of water in the first instance, because by varying this nitrocellulose of widely different properties can be obtained. I have often said that by varying the concentration of the acids, their temperature, and the time of nitration one has three factors, each of which can to a certain extent influence every property of the nitrocellulose obtained. It is the custom in a major-

ity of factories to produce soluble nitrocellulose by taking equal parts of nitric acid of 75 per cent monohydrate and sulphuric acid of 96 per cent monohydrate and nitrating the cotton at a temperature of 40° C. This nitrating acid therefore contains 14.5 per cent of water. Yet by merely altering the proportions of acid it is quite possible to make very good soluble nitrocellulose in the cold, and some modern factories make it in this way. It seems to be very difficult, if not impossible, to obtain good and stable completely insoluble nitrocellulose from wood pulp.

It is now recognized on all sides that there are no definite stages of nitration in nitrocellulose, but that the change in composition goes on without a break, if the conditions are suitable. The manufacturer of gun cotton and nitrocellulose is face to face with great difficulties. Almost everything he does tends to act detrimentally. From the nitration his nitrocellulose contains a number of lower nitro compounds, nitrated oxycellulose and hydrocellulose, nitrosaccharoses, etc., which he has to get rid of. The usual way to do this is to boil the nitro cotton for a long time. It is not quite clear why one should keep on boiling the long and closed-up fibers of unpulped gun cotton for, say, fifty hours, as is done in some factories. One would imagine that if after a preliminary washing or boiling the gun cotton were pulped and then boiled this could be done much quicker. As a matter of fact, I have found that by heating the gun cotton whilst pulping the increase in stability is very much accelerated, and several factories use the method with advantage. In France they boil for one hundred hours, and I have quite lately seen nitrocellulose that was boiled for two hundred hours without, however, being much the better for it. It must, however, be mentioned that the Waltham Abbey gun cotton as at present made is a very stable and good gun cotton, as judged both by the iodide test and by the destructive test, of which more will be said later on. This is due, in the first instance, to an investigation carried out by Doctor Robertson. He showed that the former method of giving short boilings of two hours and following them up with long boilings of eight and twelve hours was erroneous, and that two long boilings of twelve hours each would liberate acid from the nitrocellulose, giving an acid water which hydrolizes all the impurities without attacking the gun cotton itself, and that subsequent short washings are useful in eliminating the products of hydrolysis. Having had frequent occasion to put Doctor Robertson's principles to a practical test, I consider it to be one of the most useful pieces of work accomplished since the invention of gun cotton.

Messrs. Selwig and Lange, of Braunschweig, have invented the so-called "nitrating centrifugal machine," wherein the cotton is dipped and allowed to stand for the requisite time, and, the nitration being

complete, the centrifugal is set in motion and the acid wrung out. In other words, the removal of the nitrocotton and nitrating acids from the pots into the centrifugal machines is avoided. I am perhaps an heretic, but I have never been able to see the advantage of these nitrating centrifugal machines. They cost a great deal of money; they are liable to get out of order; one can only nitrate about 8 kilograms of cotton in each, and with a nitrating period of, say, half an hour, one can at the best make 10 charges a day in each; further, if the nitrating time is an hour, the number of nitrations is about 7 only. This means that for a fairly large production one requires a large number of centrifugals, and it is easy to calculate what this would mean in an artificial silk factory producing, say, 3 tons of nitrocellulose per day. The quantity of acid used for nitration must be greater, because the space between the basket containing the cotton and the jacket of the machine has to be filled up with acid, and similarly there are a good many other disadvantages. There is no difficulty in arranging pots or basins in such a way that the fumes arising from them are led away by means of an earthenware fan into an absorbing tower, just as is done in nitrating centrifugals and discharging these nitrating vessels into a wringing machine without its being necessary to expose the workmen to fumes or spilt acid. Such factories have been working very many years and give every satisfaction.

Since there is an excess of waste acid produced in revivification, this waste acid is sometimes denitrated in the same way as the acid from nitroglycerin manufacture, but may more advantageously be used in manufacturing fresh nitric acid, because in this case the nitric acid contained in the waste acid is recovered as pure monohydrate.

Revivification is nowadays very frequently carried out with sulphuric acid containing 20 per cent of sulphuric anhydride (oleum).

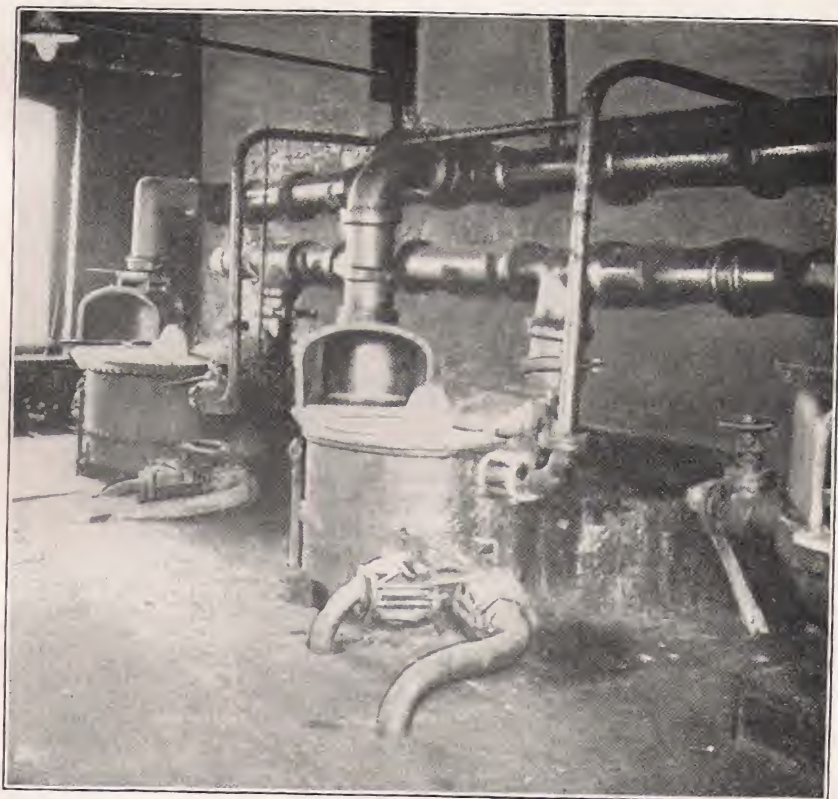
When the gun cotton is pulped and finished it is frequently packed and pressed into boxes. Gun cotton can become moldy on the outside through fungi and, according to v. Förster, have its structure destroyed;^a and v. Förster found this was promoted by paper in the cases, whilst Malenkowicz^b showed this to be due to moisture acting on the wood of the boxes. It is very important to select proper packing material on account of the possibility of detrimentally influencing the stability.

A new process for the nitration of cotton is due to Messrs. James Milne Thomson and William Thomson, of Waltham Abbey,^c and it has already been introduced in some factories. An earthenware funnel-shaped vessel can be connected at its stem by means of cocks,

^a Max v. Förster, "Versuche mit comprimierter Schiessbaumwolle," Berlin, 1883, p. 11.

^b "Mittheilungen über Gegenstände des Artilleriewesens," 1907, p. 599.

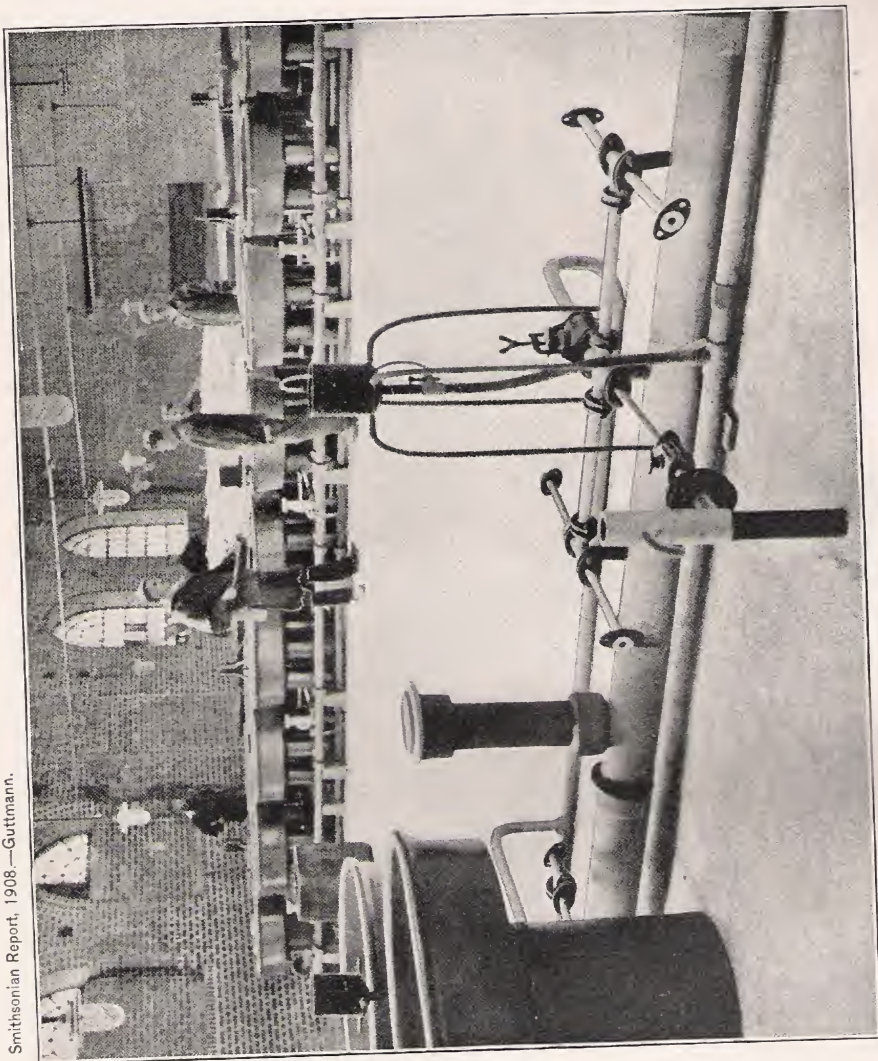
^c British patent No. 8278, of 1903.



NITRATING CENTRIFUGALS.

PLATE 4.

Smithsonian Report, 1908.—Guttman.



NITRATION OF COTTON (THOMSON'S PATENT DISPLACEMENT PROCESS).

either with a pipe supplying fresh acid or with a discharge pipe. An earthenware grating closes the opening of the stem, the new acid is introduced, the cotton dipped in it in the usual way, and then segments made of perforated earthenware plates are laid on top so as to immerse the cotton completely. A small vessel with four outlets is now laid on top, and a Segner wheel distributes water evenly into it, and this is so regulated as to flow out quite slowly and lay itself on the top of the acid without disturbing the latter. This layer of water retains all fumes that may arise from the acid, so that the air in the room is quite good. When nitration is finished water is again allowed to run in, but at the same time connection is made with the outlet pipe, and, the flow of the water being carefully regulated, it gradually displaces the acid. Finally the nitrocotton can be given a preliminary washing.

This process gives very good results, and is very convenient for making gun cotton as required for the British Government, which contains a fairly large percentage of soluble nitrocellulose. As yet there are hardly sufficient data available to decide whether the displacement process will give equally good results for gun cotton with a small percentage of soluble, or, what is far more important for smokeless powder, whether it will enable a soluble nitrocellulose with definite properties to be made, which, as is known, is always a somewhat difficult matter.

It was somewhat of a surprise when Arthur Hough, of New York,^a announced that he could nitrate starch so as to contain at least 16 per cent of nitrogen. You will remember that Hoitsema^b has already studied the possibility of producing higher cellulose nitrates than hexanitrocellulose by keeping up the strength of the acid with phosphoric anhydride. Hough seems to have found the practical solution. This nitro-starch has been utilized in the manufacture of smokeless powders, and I understand that it is used to a certain extent in the United States Army.

III.

In the year 1580 Michel Eyquem de Montaigne, in his "Essais," wrote with reference to gunpowder: "Except to astonish the ears, to which by now everybody is accustomed, I believe this is a weapon of very little effect, and I hope that we shall one day give up its use."^c Would anybody have dared to repeat such a thought thirty years ago? Yet it has come true.

^a British patent No. 12627, of 1904.

^b "Zeitschrift für angewandte Chemie," 1898, p. 273.

^c "Sauf l'étonnement des oreilles, à quoy désormais chacun est apprivoisé, je crois que c'est une arme de fort peu d'effect et espère que nous en quittons un jour l'usage."

About the year 1410 we find that quaint treatise on gunpowder called "Feuerwerksbuch," said to have been written by a master gunner, Abraham von Memmingen. It contains the famous history of how Berthold Schwarz tried to make a gold paint and invented gunpowder and guns instead. This book was lent to other master gunners, who severally copied and enlarged it, until in 1534 it was printed in Frankfort on the Main under the title, "Büchsenmeyersterei." In this printed edition we find a prescription, "how to shoot out of a gun as far with water as with gunpowder." Take 6 parts of nitric acid, 2 parts of sulphuric acid, 3 parts of liquid ammonia, and 2 parts of "oleum benedictum" (crude tar oil), and charge the gun to a tenth part of its bore. It further advises quaintly, "Light it quickly, so as to get away in time. See that the gun is very strong. With an ordinary gun you can shoot 3,000 paces with this water, but it is splendid." This is the first evidence of a nitrated organic substance having been used as a propellant.

I have already alluded to the history of the invention of gun cotton, but one reference remains to be given, showing how early the use of gun cotton in rifles was thought of. It is known that Schönbein reported on his gun cotton on March 11, 1846, and on May 27, 1846, he made experiments with rifles. Professor Otto, of Brunswick, had, independently of Schönbein, also made gun cotton, and published his results on October 5, 1846. He also tried gun cotton in a rifle, and Doctor Hartig published a pamphlet in 1847 at Brunswick, under the title "Untersuchungen über den Bestand und die Wirkungen der explosiven Baumwolle" (Experiments on the Condition and Effects of Explosive Cotton), and therein he makes a statement, which has since attained great importance. He says that the effect which acetic ether has on "the shooting fiber" is very remarkable. He has found that if he makes a stiff, clear jelly with this ether from the shooting fiber, it does not alter its chemical state, and if put in a thin layer on a plate of glass, a snow-white residue is left after the ether has evaporated. If this residue is put into dilute alcohol and then dried it will have in every respect the same properties as the shooting fiber. He mentions already that probably on account of the altered state of aggregation there is a considerable diminution of the explosive force.

Nothing was heard of a real powder made of nitrocellulose for a very long time. It is true that in 1847 the Commission de Pyroxylye, which was appointed in France, "experimented with it in every form, as wadding, spun, twisted, woven, reduced to powder by the action of paper makers' cylinders, felted together by means of dextrine, finally granulated like cannon powder,"^a but it was too violent for

^a "Note sur la pyroxyline ou coton-poudre," par M. Susane, Mémoires de l'Académie Impériale de Metz, 1855.

use in guns and rifles. Baron von Lenck, in Austria, made gun charges from fibrous gun cotton, and we know that they were not a success. In 1865 Capt. Eduard Schultze, of Berlin, published a pamphlet on his "new chemical gunpowder," in which he gave the first indication of his powder, but more words than details. At the same time, however, a number of German journals published some particulars of its manufacture. Very soon after Schultze used finely pulped nitrocellulose, and made powder grains by agglomeration with water in drums. It is also remarkable that in 1865 Abel^a patented the production of grains of gun cotton by placing a mixture of gun cotton with water and a little gum arabic in a pan, and giving it a shaking motion, whereby the gun cotton was formed into grains. He also proposed to mix soluble and insoluble gun cotton, and to make the soluble gun cotton serve as a binding material by treatment with wood spirit, alcohol, ether, or mixtures of these liquids. It is further interesting that Doctor Kellner, of Woolwich, is mentioned in a German book which appeared in 1866^b to have been the first to succeed in making a granular smokeless powder. Neither Abel nor Kellner seem to have continued at the gelatinization of nitrocellulose.

The author well remembers, however, a firm in Marchegg, near Vienna, which existed under the name of Volkmann's k.k. priv. Colloidinfabriks Gesellschaft H. Pernice & Co. They originally bought the patent for the Schultze powder, and made it under the name of nitroxylin. From 1872 to 1875 they made a powder called collodin, the invention of Friedrich Volkmann, which was patented under date November 8, 1870, and May 31, 1871. After three years of existence the Austrian Government ordered the works to be closed, because they claimed that this explosive was infringing their gunpowder monopoly.

Volkmann cut up alder wood into small grains of the size of black powder, boiled, and washed, then bleached them, and after final boiling nitrated them in a mixture of nitric and sulphuric acid. Thus far the treatment was that usually given to cotton waste. The finished grains were soaked in a solution of potassium nitrate, or of potassium nitrate and barium nitrate, and, after drying, treated with a mixture of 5 volumes of ether to 1 volume of alcohol. The solvent was allowed to penetrate the grains completely, and the more the substance was dissolved the more the volume decreased. On taking the powder out of the solvent it had the appearance of a mush, which, after twelve hours' drying at 30° C., was converted into a dough, a pasty, pliable substance, from which any shape could be obtained by molding and pressing. Volkmann seems to have known everything about a smokeless powder.

^a British patent No. 1102, of 1865.

^b "Buch der Erfindungen," Leipsic, 1866, chapter on gunpowder and arms.

In 1882 Mr. Walter F. Reid patented ^a the agglomeration of nitrocellulose into grains and moistening them with ether alcohol for the purpose of hardening the grains. I had the advantage of seeing this manufacture and some experiments with this powder in 1883, in which year also Oscar Wolff and Max von Förster published and patented ^b the method of coating small cubes of gun cotton with a solvent for the purpose of keeping them permanently moist. Mr. Reid's powder is manufactured under the name of E. C. powder, and is still a favorite sporting powder, but, being what is now called a bulk powder, namely, a powder of very loose structure and low volumetric density, it was too violent in its effects for military rifles, while for sporting rifles it was just the right thing. I would again mention here that in the beginning of 1886 I suggested to Professor Hebler, the well-known Swiss pioneer of the small-bore rifle, the use of a piece of blasting gelatin as a charge for a rifle cartridge,^c but that the very idea frightened him, although he wished to have a pellet of compressed gun cotton from me for the purpose. Vieille in 1886 ^d thoroughly gelatinized nitrocellulose and made sheets of it, which he cut up in strips or small lozenge-like squares. This was the first military smokeless powder. It has been said that Vieille made his discovery while trying to make a bulk powder similar to E. C. powder, but I have it from him that his invention was the outcome of prolonged study and experiment.

This impartial survey shows that while the merit of making the first powder-like material from a nitro compound belongs to Hartig, and while Schultze made the first commercial powder, yet the invention of a gelatinized powder in the modern sense must be attributed to Friedrich Volkmann, although, independently of him, Reid rediscovered, twelve years later, a hardened sporting powder, and Vieille, sixteen years later, a thoroughly gelatinized military powder.

Nitroglycerin-nitrocellulose powder was invented by Alfred Nobel in 1888,^e who gave it the name of ballistite. The British Government adopted a powder which contained insoluble gun cotton with nitroglycerin and vaseline, the whole being dissolved in acetone.^f Ballistite is the service powder in Italy and is much used for large guns. Aniline is now added, and it is claimed both for vaseline, aniline, and diphenylamine that they exert a great stabilizing influence on the powder.

^a British patent No. 619, of 1882.

^b Id., No. 3866, of 1883.

^c Journal of the Society of Chemical Industry, 1894, p. 575.

^d Mémorial des Poudres et Salpêtres, 1890, p. 9.

^e British patent No. 1471, of 1888.

^f Id., No. 5614, of 1889.

There is no need for me to detail the manufacture of powders. Nitrocellulose powders are made from dry nitrocellulose, in a mixing machine, using a solvent (generally ether alcohol or ether acetone). In many factories the nitrocellulose is made anhydrous by soaking it in alcohol, and then squeezing it out in a press. Some think that the quality of the powder is affected by this method. Some have found a loss of substance up to 5 per cent to take place with certain nitrocottons. The mixture is then rolled under a pair of heavy rolls into sheets of the required thickness, cutting them up into squares, and afterwards drying these. In some services ribbons are used instead of grains, and in others threads or tubes are made of such powder and cut into sticks of the length required for the charge. In Germany camphor was formerly added to the powder while kneading it. Some countries leave a certain amount of the solvent in the powder, and formerly in France a little amyl alcohol was added, while now diphenylamine has been adopted; this was already used in 1889 in Germany for C/89 powder made by the Cologne-Rottweil factory.

Ballistite is made in a different way. Soluble nitrocellulose in the shape of a fine powder is suspended in fifteen times its own bulk of water and nitroglycerin added, the mixture being stirred by means of compressed air. This causes the nitroglycerin to dissolve up the nitrocellulose, the water acting as a carrier only. The paste resulting in this way is then brought under steam-heated rolls, weighted to exert a pressure of 100 atmospheres, to thoroughly incorporate it, and then mixed by rolling the sheets over and over until they are quite satisfactory. The sheets so obtained are then cut up into flakes, cubes, strips, etc., as required.

You will readily understand that every weapon may, and generally does, require a different powder in order to give the desired velocity and not to exceed the permissible limits of pressure. It is obvious that it would be very easy to alter the composition in every case, but as a matter of course such an expedient would be quite undesirable alike from a manufacturing and from a service point of view. Hence already in the days of black powder it has been the custom to vary the shape and size of the powder. We thus have ribbons in France, strings in Great Britain, flakes and tubes in Germany, cords of square section in Italy, short multiperforated cylinders in the United States, cubes from ballistite, spiral sporting powder in Germany, the *poudre peigne* (spiral powder with comb-shaped incisions) of French inventors, etc. Further, these powders may then be made in various lengths, breadths, or thicknesses, and with various kinds of holes, incisions, etc. It is quite impossible to generalize and to say that a particular form is good or bad, because it probably does suit a special weapon. It is a fact that up to a certain size round

grains are most likely to give good combustion, and that cord or tube comes next; on the other hand, a flat ribbon is likely to burn more uniformly, although, again, a variation in the rate of combustion at different intervals of time may just be what is wanted.

The conviction has grown of late that in addition to being smokeless a powder should also be flameless, so as not to disclose the position of an attacking force.

The military powders suffer, in the first instance, from irregular shooting. In the case of sporting powder, it is necessary to carry out shooting tests with every small batch, because the reputation of a firm depends on keeping powder out of the market which is in the slightest degree deficient. Careful blending has to be resorted to in order to obtain absolutely uniform results throughout.

Of other difficulties in manufacture I will mention only a few. The treatment of a powder under rolls is to a certain extent guided by rule of thumb. It is all very well to look through the paste, the sheet may appear quite transparent to a good and experienced eye, yet small nodules of nitrocellulose may have escaped solution for a long time. The constant crackling heard when rolling thin sheets plainly points to such isolated and undissolved fibers. Incorporating in a kneading machine does not improve matters. Pressing powder out of a die gives very good results with small diameters, but with larger diameters very much depends upon the shape of and the wear on the nozzle, its position among several others or relatively to the die, and on whether the outer skin will contain air bubbles or be cracked. If too much solvent is taken, or the proportions of a composite solvent are not quite suitable, the density and uniformity of the powder will suffer. One of the greatest difficulties lies in the proper drying of powder. The smaller sizes of sticks, ribbons, tubes, etc., are easier to deal with. The larger and thicker ones, however, sometimes require months to dry properly. With some powders this defect is to a certain extent avoided by leaving some of the solvent behind, but then, of course, we have on the one hand the difficulty of not knowing exactly when the correct amount of solvent is present, and, on the other hand, a certain amount of risk in that the powder would in course of time undergo changes by gradual evaporation of the solvent.

Sporting powders are of two kinds, the so-called "bulk" powders, consisting of loose granules, coated or hardened by means of a solvent, and the so-called "condensed" powders, gelatinized throughout, and made in practically the same way as military flake powders.^a The former are supposed to just fill a cartridge used in the old black-

^a The micro-photographs reproduced on plates 5 and 6 were kindly prepared by Mr. Henry de Mosenthal.

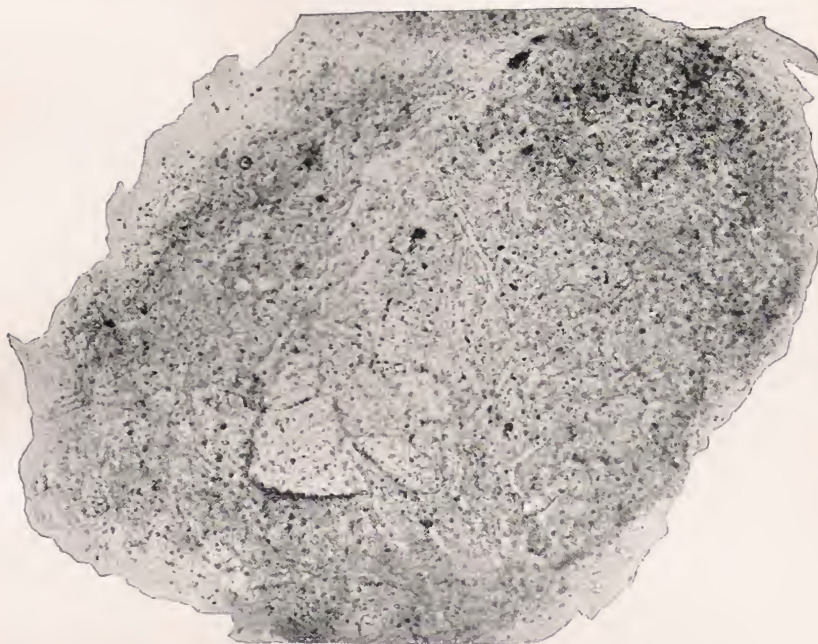


FIG. 1.—SMOKELESS BULK POWDER SEEN UNDER THE MICROSCOPE
IN ORDINARY LIGHT.

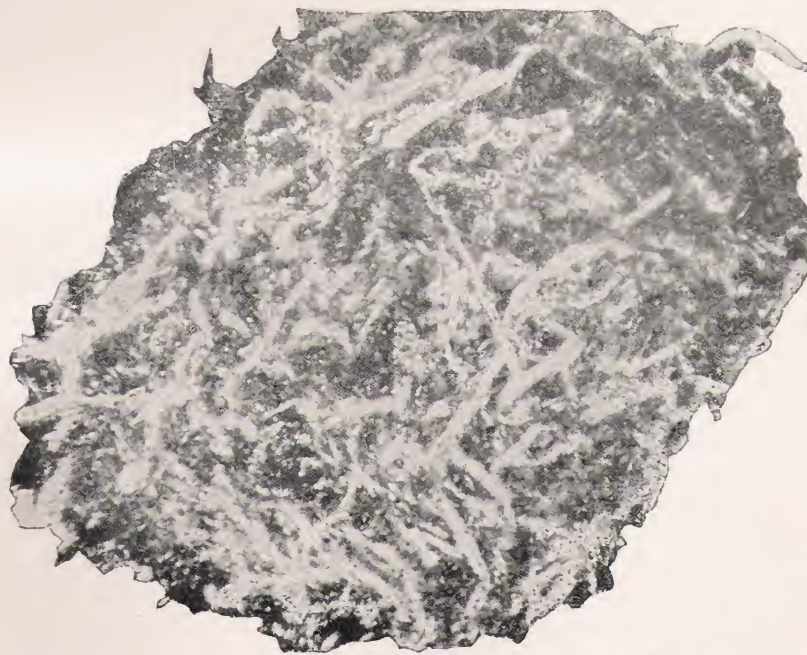


FIG. 2.—SMOKELESS BULK POWDER SEEN UNDER THE MICROSCOPE
IN POLARIZED LIGHT.

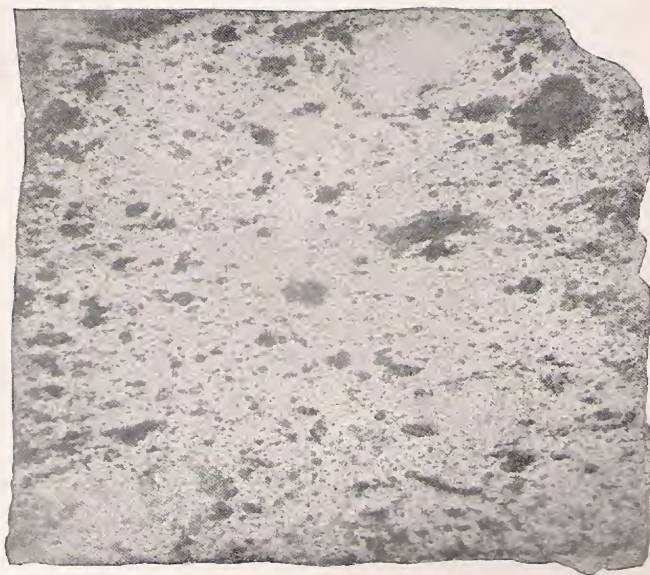


FIG. 1.—SMOKELESS FLAKE POWDER SEEN UNDER THE MICROSCOPE IN ORDINARY LIGHT.

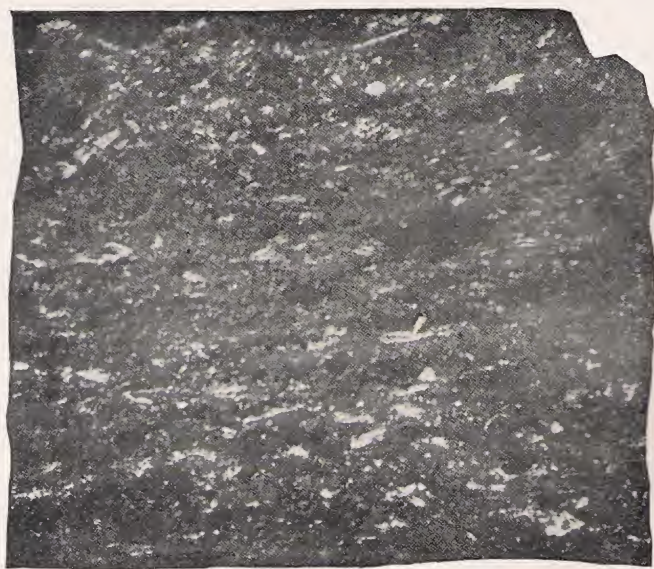


FIG. 2.—SMOKELESS FLAKE POWDER SEEN UNDER THE MICROSCOPE IN POLARIZED LIGHT.

powder gun; the latter are made for modern weapons. The usual "bulk" powders are composed of soluble nitrocotton mixed with potassium or barium nitrate, and generally worked up in an incorporating mill or drum. The mixture is then either sprinkled with water in a rotating drum, so as to form grains, or extended on a shaking table making short and rapid oscillations. Alternatively it may be put into an hydraulic press and then broken into grains, the solvent being in every case sprinkled over when the grains are already formed.

The "condensed" powders are usually made by rolling the "paste" into very thin sheets (0.1 millimeter and less), which are then cut into small flakes to obtain the requisite rapidity of combustion. Such powders are dried fairly quickly, and they may sometimes even be boiled in water to promote elimination of the solvent.

Since 1800, when Howard invented fulminate of mercury, and since 1815, when Joseph Egg made the first cap, but little progress has been made in the manufacture of these articles. It is still the usual cap and the usual detonator, the only difference being that potassium chlorate enters partly into the composition of detonators, whilst for smokeless powders a hotter flame is found essential, and is obtained by adding a combustible substance. Aluminum powder, either mixed with the fulminate or pressed in a layer on top of it, has been successfully employed.^a The Rheinisch-Westfälische Gesellschaft of Troisdorf make now detonators of tetranitromethylaniline (called tetryl).^b It is said that quite half of all the detonators at present manufactured in Germany are made with trinitrotoluene.

The manufacture of fulminate of mercury is performed in almost the same way as that described fifty years ago.

The increasing demand for ammonium nitrate safety explosives has resulted in the use of greater quantities of powerful detonators. For the same reason great progress has been made with electric detonators. Formerly high-tension fuses fired by frictional electric machines were almost solely used, and Breguets were the only low-tension fuses employed in mines. Nowadays the tendency is to use low-tension fuses and magneto-firing apparatus, thus greatly reducing the risk of firing the pit gases.

Bickford's invention still holds the field as regards safety fuses. I have explained in my first lecture wherein the few improvements consist that were made on safety fuses. It is curious that all attempts to make a safety fuse with a core of smokeless powder or some other nitro compound have so far been unsatisfactory. It seems impossible to insure uninterrupted burning. Of late, rapid-burning fuses

^a British patent No. 23366, of 1904.

^b Id. No. 13340, of 1905.

were introduced, some being fired in groups by means of pistols and other central-firing arrangements. General Lauer and Mr. Tirmann introduced friction fuses, which are fired by means of wires from a distance, and are extensively used chiefly in Austrian coal mines. Girard made "cordeaux détonants" by filling lead tubes with nitrohydrocellulose and then drawing them out to the diameter of an ordinary safety fuse. In 1906 these fuses were filled with melinite, and now trinitrotoluene is also used, which permits the employment of lead tubes instead of the costly tin tubes indispensable with a picric acid explosive.^a The most perfect fuse of this kind is, however, the instantaneous fuse invented by General Hess and introduced into the Austro-Hungarian service. Originally it consisted of a mercuric fulminate core on four threads. In 1903 Hess "phlegmatized" the fulminate^b by the addition of 20 per cent of hard paraffin, but a number of such fuses, tied together by knots, can be detonated by a common detonator, thus replacing electric shot firing and dispensing with a detonator in each bore hole. The fuse can be cut, hammered, squeezed, etc., without danger.

The more industry progressed all over the world, the greater the coal consumption became, and the more frequently occurred those appalling mine disasters which from time to time convulse public feeling. The British Government was the first to nominate a fire-damp commission. Then followed commissions in Prussia, France, Saxony, and Austria, but not one of them tried a safety explosive before September, 1885. The Prussian Government, however, had built a testing station and trial gallery at Neunkirchen, in the beginning of September, 1885, under the direction of Mr. Margraf. In September, 1887, a carbonite consisting of saltpeter, cellulose, nitroglycerin, and sulphureted oil was found to be absolutely safe. In 1886 Margraf tested securite against carbonite, and this also was found safe. In April, 1887, roburite and kinetite were tried, and in August, 1887, soda dynamite. Thus carbonite was really the first safety explosive.

It is necessary to distinguish between explosives which are safe in manipulation (*handhabungssicher*) and such that are safe in fire damp (*wettersicher*). The latter only are called safety explosives in this country.

The obvious question is, What makes an explosive safe in fire damp? I confess that, having most carefully examined the views of those most competent to give an opinion, I fail to find a definite answer. At one time the Prussian commission stated that the more rapid the explosion the safer the explosive, and some color is lent to

^a *Artilleristische Monatshefte*, August, 1908.

^b "Mittheilungen über Gegenstände des Artillerie und Geniewesens," 1907, p. 115.

this theory by the fact that fulminate of mercury does not ordinarily ignite fire damp, whilst black powder always does. The theory is, however, controverted by certain black-powder mixtures, foremost among which is bobbinite, which is safe up to a certain point, and by nitroglycerin and blasting gelatin, which are not.

The French Government commission stated that an explosive whose temperature of explosion was below $1,500^{\circ}$ C. could be licensed for use in fiery mines. Curiously enough carbonite, so far the safest of all, and several others, which are licensed for such use, have a temperature of explosion considerably higher than $1,500^{\circ}$ C.

Mr. Bichel, in conjunction with his collaborator, Doctor Mettegang, says that the velocity of detonation, the maximum temperature of the products of combustion, the length and the duration of the flame of an explosive all influence the safety of an explosive adversely.^a He considers, and in the author's opinion very justly, the nature of the products of combustion to be all important, whether they consist of solid particles which remain incandescent for a considerable time, or of large quantities of combustible gases shot forward with great force. In this way he corroborates early attempts to photograph the flame of an explosion made by Schoeneweg, the inventor of securite, and by Siersch, of Pozsony. The velocity of detonation can not, however, be considered to be a determining factor under all circumstances. Certain nitroglycerin explosives, amongst which we may also include carbonite, explode much more rapidly than, say, bobbinite, and yet show themselves to be much safer when tested. I myself have found that up to a certain point the addition of picric acid gave increased safety on test.

It will be remembered that the British commission found a water jacket round the charge very efficient. Sodium carbonate, magnesium sulphate, and other substances were tried, either separately in front of the explosive or as ingredients. More prominence was then given to the French recommendations, and the notion became prevalent that the addition to the explosive must be a flame-cooling agent in the shape of water vapor or some other heat-absorbing gas. Thus permanganate, bichromate oxalates, and other salts were used, and of late common salt has sprung into favor.

The only definite result obtained so far is that ammonium nitrate is absolutely safe in all quantities, and that cellulose and sinular substances in nitroglycerin compositions—e. g., rye flour in carbonites or wood pulp in other explosives—renders them highly inert in fire-damp mixtures. Ammonium nitrate can not, however, be used by itself, although Lobry de Bruyn succeeded in exploding it,^b and therefore some combustible substance must be added. It simply

^a Glückauf, 1904, No. 35.

^b Recueil des travaux chimiques des Pays-Bas, 1891, p. 127.

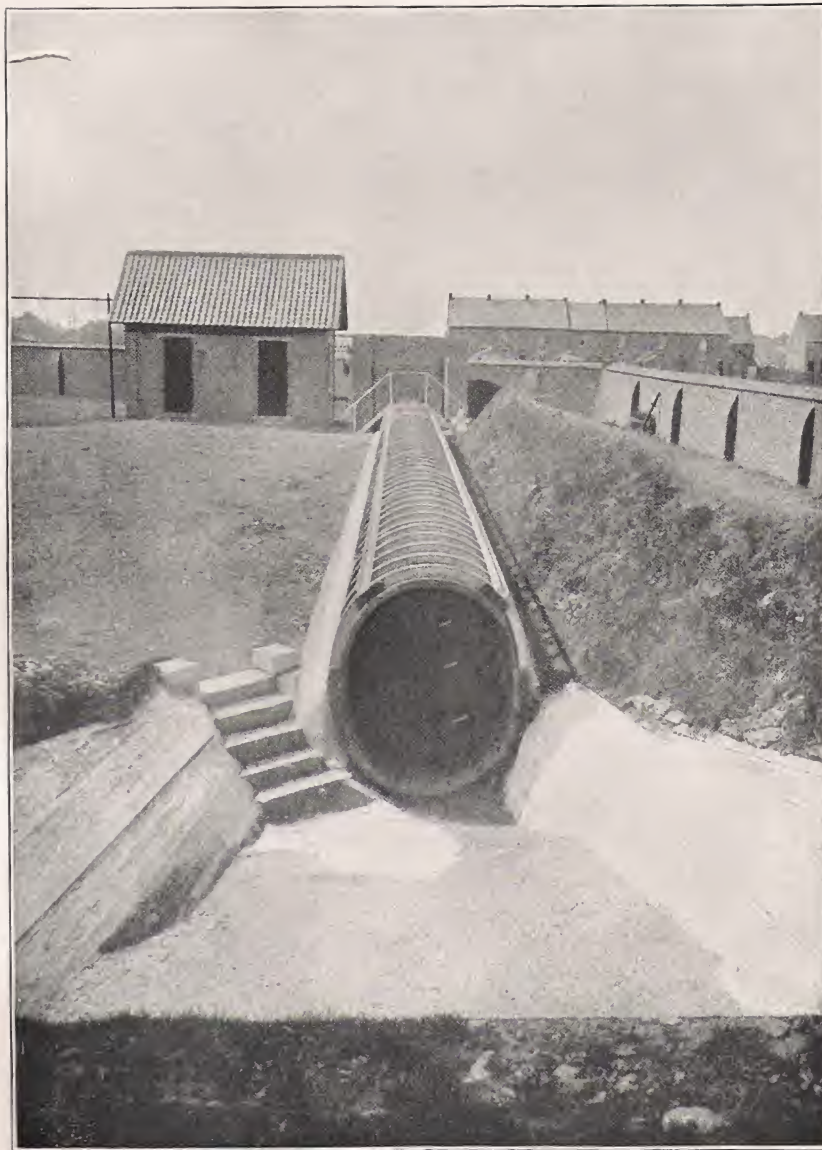
remains to be determined what minimum quantity of such combustible can be added to avoid flames of great length and duration.

The next question is, How can one tell whether an explosive is "safe"? This question is a still more difficult one to answer. The various governments and also certain factories have erected testing stations. These stations generally consist of a long wooden or iron tunnel, round or oval in section. The explosive is shot into a gas mixture. In this country a ballistic pendulum is used to ascertain the quantity of the explosive equal in force to 4 ounces of dynamite No. 1, and this quantity with a stemmed shot is then fired in air containing 15 per cent of coal gas. If the mixture does not fire in 20 shots the explosive is considered a safe one. In most other countries the quantity of the explosive in question is determined which will fire and that which will just not fire a certain pit gas mixture. This gives us what Mr. Watteyne, the well-known Belgian authority, calls the "charge limite" of an explosive. This latter way is certainly the more rational one, since it permits of comparison between different kinds of explosives. Is this method of testing, however, above reproach? I think not, although I know of no better one at present. It has been found that the narrower the bore of the cannon the easier ignition takes place under certain circumstances. The Woolwich circular section gallery, which has a sectional area of 0.36 square meter, is much more sensitive than the elliptical Belgian one, whose sectional area is 2 square meters, and, in fact, even with equal diameters each gallery may be said to have its own ignition temperament, which affects the results. Thus quite recent tests at Frameries in a gallery having a sectional area of 0.28 square meter showed that two safety explosives, whose charge limite was 900 and 450 grams, respectively, fired at 300 and at 75 grams. The gas used also exerts considerable influence on the tests.

It has been known for a long time that coal dust as well as pit gas is highly explosive. I believe that Engler, when investigating explosions in the charcoal heaps of the Black Forest,^a was the first to show that mixtures of coal gas and air, so poor in gas as to be non-inflammable, were rendered explosive by the addition of some charcoal dust. The Mining Association of Great Britain took the lead, experimentally investigating the influence of coal dust on explosions in mines. An iron shell 7 feet 6 inches in diameter and 1,083 feet long was used to carry out the experiments. So far it has already been ascertained^b that two zones of stone dust on either side of a zone of coal dust arrested the path of a flame, and that unless the coal-dust zone exceeded 180 feet in length, no explosive force was mani-

^a *Chemische Industrie*, 1885, No. 6.

^b "Coal dust experiments," *The Times*, September 24, 1908.



TESTING STATION AT FRAMERIES (END VIEW).



TESTING STATION AT FRAMERIES (VIEW OF THE INTERIOR).

fested. Might I submit an old idea, which I base on some patents of mine that have proved highly useful? An absorption tower retains solid particles contained in a gas mixture, and also cools the latter very efficiently, and one of the best methods for absorption has proved to be the production of a fine spray or mist of moisture. It seems quite feasible to utilize certain lengths of tunnel for the construction of inverted absorption towers at intervals, and certainly at every point where a side gallery runs into the main or haulage roads. So much seems certain to me from the study of the results of past investigators that a small addition of coal dust will be found to promote the explosion of poor gas mixtures, and that, therefore, a separation of the dust from the gas will in some cases prevent an explosion.

Lacking definite knowledge as to what renders an explosive safe in fire damp, and how this is to be ascertained, it would be natural to seek a solution in practical results. The sale of an article does not always depend upon its real value, but very frequently on the way it is advertised and pushed, whether it is made in the country of consumption or not, whether it possesses disadvantages that render another less efficient article a preferable one, etc. In spite of this it is not unfair to assume that the statistics showing the quantities of safety explosives actually consumed in a great coal-producing country like Great Britain have a real bearing on the question as to which explosives have given a reasonable amount of safety. The report of the inspectors of explosives for 1907 gives the following highly instructive figures: Out of a total consumption of 7,764,122 pounds, were used, of saxonite, 1,721,193 pounds, or 22.18 per cent, and of bobbinite, 1,063,111 pounds, or 13.69 per cent.

Saxonite contains a large percentage of nitroglycerin. Bobbinite is a black powder mixture.

From the inquiry on bobbinite^a the following table regarding accidents in coal mines caused by various safety explosives in 1904 and 1905 is calculated:

	Con- sump- tion.	Accidents.		Killed.		Injured.	
	Per cent.	Number.	Per cent.	Number.	Per cent.	Number.	Per cent.
Bobbinite.....	13.69	20	17.54	2	8.33	30	18.87
Other permitted explosives.....	86.31	94	82.46	22	91.67	129	81.13

It will thus be seen that a black powder mixture like bobbinite, which would not be licensed in any other country and be condemned without trial, ranks second in consumption, being used to the extent

^a Report of the departmental committee on bobbinite, London, 1907.

of 13.7 per cent of the total consumption, while saxonite, a nitro-glycerin explosive, ranks first, with 22.18 per cent of the total.

Am I therefore right in saying that we have succeeded in making the use of explosives in coal mines infinitely more safe than before, but that we do not really know why?

IV.

Nitrocellulose has found a greater sphere of use for purposes other than smokeless powder or dynamites. The celluloid industry, introduced by the Brothers Hyatt, and more recently the artificial silk industry, consume enormous quantities. Of celluloid the United States produce about 4,000 tons per annum, Germany 15,000, and the rest of the world about 5,000 tons, of which yearly total of 24,000 tons this country produces about 2 per cent. This necessitates about 14,000 tons of nitrocellulose per annum. Of artificial silk, about 5,000 tons are made annually, though only about 200 tons in England.^a The amounts used for varnishes like pegamoid, fabrikoid, etc., for making or steeping incandescent gas mantles, for waterproofing solutions, for patent leather (nitrocellulose dissolved in amylacetate, and mixed with aniline black) and for photography are also considerable. The solubility of the nitrocellulose in a definite mixture of ether alcohol to the extent of 2 per cent either way is by no means unimportant, as this may mean 10 per cent more of very expensive solvent. When you consider that one of these factories, which I had occasion to revisit quite recently, makes as much as 3,000 kilograms of silk a day, you will have some idea of the sums involved.

In neither of these cases is the nitrocellulose pulped, but the whole of the fiber is dissolved. I am afraid purification is sometimes not carried as far as it ought to be with due regard to the stability of the finished celluloid. In the case of artificial silk the fact that the nitrocellulose is denitrated seems to indicate that thorough purification is unnecessary, but the silk fiber made from well-stabilized nitrocellulose will be found to possess inherent good properties of its own. The same may be said of varnish, although in this case a slight acidity at certain stages of the process has the advantage of rendering the nitrocellulose more readily soluble.

The manufacture of these nitrocelluloses also varies in other respects. In dealing with such large quantities everything is carried out expeditiously and without much handling. The nitrocellulose for

^a According to Dr. Richard Schwarz, there are at present in Europe 30 factories making artificial silk, and the world's production in 1907 amounted to 3,300,000 kilograms, of which 1,500,000 were nitrocellulose silk, 1,300,000 "Glanzstoff," and 500,000 viscose silk (Neue Freie Presse, Vienna, January 5, 1909).

artificial silk is not fully dried, but from 12 to 30 per cent of water is allowed to remain in it.

For the sake of completeness mention must be made of the proposed use of explosives for motive power. I well remember having shown me at Vienna, in 1878, an engine to be worked by small charges of dynamite. In order to show the absence of danger the inventor had made the model entirely of wood. Again, quite recently my advice was sought regarding the application of smokeless powder to flying machines. Several patents referring to motors and compressors driven by explosives have been taken out, and one of them quite recently.^a

An account of progress on explosives would be incomplete without mention of the conditions under which they are manufactured.

The late Col. Sir Vivian Dering Majendie deserves lasting recognition for having created that most excellent explosives act of 1875. The influence of this act, and perhaps almost to the same extent of the annual reports of the British inspectors of explosives on the arrangements and construction of buildings and machinery, the general cleanliness of the operations performed, and the security of workmen against accident can hardly be overrated, and the example set in this country has been followed all over the world.

In arranging buildings due consideration is now paid to the dangers present on account of the nature of the operation and the quantity of materials dealt with. The advent of high explosives has unfortunately made us acquainted with effects of explosions unknown in the old powder days, and in order to counteract these effects the author recently suggested ^b the construction of danger buildings in a special kind of ferro-concrete. The buildings are so designed that pieces of burning débris can not penetrate their roofs, and so bring about their destruction. At the same time the shock of the explosion transmitted from a distance through the ground will not cause the walls to open out. This proposal has been very favorably received by a number of manufacturers, and in several instances has already been adopted. The armoring of such a building forms a Faraday's cage, and renders the whole structure lightning proof. This is of importance, since the regulations governing the erection of lightning conductors have not increased the safety of buildings to any great extent in spite of lightning-rod conferences and investigations. Magazines which were satisfactorily tested on the very day of a thunder-storm have been blown up, and nothing short of a cage, or at least a

^a British patents, Nos. 961, of 1874; 24742, of 1904; 28376, of 1904; 22125, of 1905.

^b "Explosions and the Building of Explosives Works," *Journal of the Society of Chemical Industry*, 1908, No. 13.

complete system of conducting network over and on the buildings, seems to be efficacious.

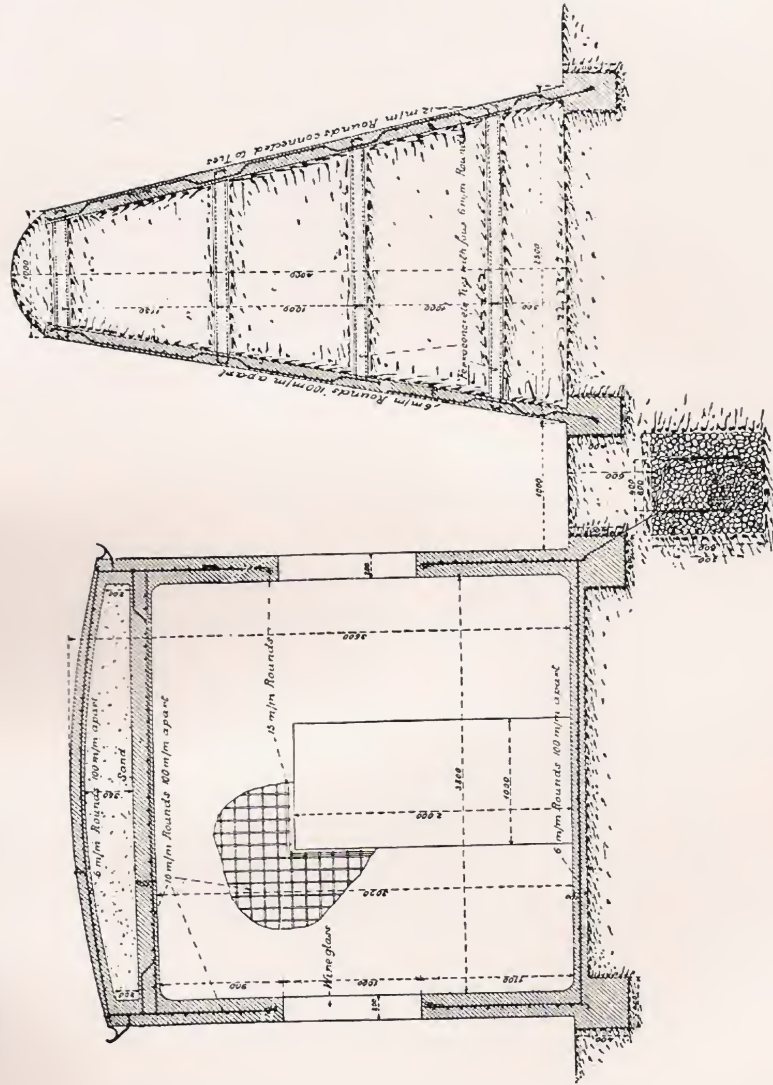
Despite all precautions disasters of great magnitude will occur in modern explosives works. This is, no doubt, in the first place, due to the fact that quantities are nowadays made in such works which were not dreamed of thirty years ago. For instance, the works at Modderfontein and Somerset West produce annually over 10,000 tons of dynamite, and several other works run them very close. Such an enormous output requires a very considerable number of buildings, and consequently the chance of damage to life and property is greatly increased. The construction of factories has, on the other hand, proceeded on somewhat orthodox lines, and not always, perhaps, with due regard to subdividing and minimizing risks.

Another reason for such catastrophes is the want of appreciation of certain inherent dangers. The author has always warned manufacturers and users alike that the function of an explosive is to explode, and that although certain compositions are almost insensitive to ordinary impulses, such as blows, friction, etc., yet he never believed that any explosive existed which under favorable conditions and by proper means could not be made to explode. It is true that continental railways carry certain explosives, like ammonium nitrate mixtures, by ordinary goods train, and the author believes this to be an example which might be quite safely followed by British railway companies in the best interests of the public. There is no danger attached to any of these explosives when in the safe custody of a railway van, and when they do not come into contact with dangerous goods.

Yet another warning to manufacturers may not be out of place. Special attention must be paid to prevent any accumulation of dirt in places liable to exposure to heat. In the French powder factory at Saint-Médard the explosion which occurred in 1891 could be clearly traced to gun-cotton dust lodging in the joints and cracks of a wooden workshop.^a Do factories even now take every precaution to prevent the accumulation of dirt of this kind? The author has reason to doubt it, and a clean-up at a factory which he witnessed a short time ago was quite an eye-opener. He can only warn those concerned that every building where explosive dust can be produced, and every appliance and utensil therein, should be periodically and thoroughly cleansed and overhauled. Imagine a drying tray, covered underneath with canvas, on which gun cotton or powder is dried all the year round, and ask yourselves what the chemical stability of the dust may be after a year's exposure to a temperature of 40° C. (some factories dry at 50° C.), and whether a material dried on such a tray is fairly treated.

^a *Mémoires des Poudres et Salpêtres*, 1894, p. 7.

Smithsonian Report, 1908.—Guttman.



EXPLOSIVES WORKSHOP AND MOUND BUILT IN FERRO-CONCRETE.



Nowadays an explosives factory seems inconceivable without electric light and small motors near buildings or on machines, while even the operation of drying sensitive compositions is performed by electric resistances serving as a perfectly adjustable source of heat.

Modern explosives have, on the other hand, introduced electrical dangers themselves. In the first lecture the possibility of firing a press charge of black powder by static electricity collecting between ebonite press plates was mentioned. Nitrocellulose is electrified by the current of warm air passing over it when drying, and the necessary earthing arrangements were first proposed by Mr. Walter F. Reid, and in many cases especially designed by the author. Mixing machines for blasting gelatine and smokeless powder, especially those provided with reversing gear and belts running in opposite directions, have been known to give long sparks unless properly earthed. This was remedied at Waltham Abbey by saturating the belts with glycerin. The powder itself during manipulation will generate electricity. Ether vapor given off from smokeless powder and mixed with air can be fired with a very small spark, and special care should be taken in preventing its formation.

The manufacture of high explosives seems a simple operation even to experienced chemists, and the danger attending the process appears to be the only difficulty. As a matter of fact, it bristles with difficulties. A good many have already been mentioned, and a few additional and special points are worthy of note.

Glycerin is a uniform, easily purified substance, and its nitric ester, nitroglycerin, although sensitive to a blow, especially when frozen, is a chemically stable explosive, tame and harnessed for the service of man. Most nitro compounds of the aromatic series have very great chemical stability.

Picric acid is a treacherous substance. It is very powerful, but that is its only recommendation. Those who use it may be asphyxiated by the fumes of a prematurely exploding shot; those who are fired at sometimes rejoice when it fails to explode. It requires special mixtures to avoid melting at high temperatures, and it attacks its metal container, forming a dangerous picrate. As an ingredient of other explosives it is useless, since on account of its acid properties it reacts upon the other ingredients. Moreover, it is capable of displacing other acids, such as nitric acid in nitrates, a disagreeable property which some patentees have found out to their cost. With Montaigne, "I hope that we shall one day give up its use."

A more inconvenient material still is nitrocotton. As already stated, cotton is one of the most complex substances known, and for some unexplained reason we have been in the habit of using it after an ill-treatment following upon an undesirable state of cleanliness. At the best, however, we have an almost uncontrollable substance in

nitrocotton. It is in such a loose state of equilibrium that the slightest reaction will upset its balance. No wonder that when nitrocellulose is mixed with another explosive like nitroglycerin to form smokeless powder it becomes less reliable, and acts detrimentally on the nitroglycerin. This is accentuated still more in the presence of another disturbing factor, such as heat or an alkali. It is a fact that any alkali, however weak, will gradually saponify the nitrocellulose, and although dangerous decomposition would rarely set in, a bad heat test may result and cause the nitrocellulose to be destroyed by the authorities. Chalk in water is no exception to this action.

The case is very much aggravated by the action of heat. It is well known that properly purified guncotton has been stored in all climates without giving rise to alarming decomposition, even when the temperature was above the normal. Nitroglycerin and nitrocellulose, both of which will by themselves give a potassium iodide heat test of, say, twenty minutes, may, however, when mixed, not stand more than ten minutes. It is a convenient excuse to say that this is due to an alteration of the physical state, but no proofs have been given for such an assertion, and I should be curious to hear of them.

The amount of nitrous acid required to color the test paper is so small (according to Will^a it is only 4×10^{-5} milligrams, equivalent to 0.0000016 per cent, or about 1 in 60,000,000 for a sample of 2.5 grams) that whatever its physical state, there would always be enough material exposed on the surface to give off this quantity of gas in regulation time if the explosive were of a low order of stability. There is much more justification for supposing that a chemical reaction goes on between the nitroglycerin and nitrocellulose at the elevated temperature of the heat test (82° C.), the nitrocellulose being first decomposed, and the nitrous gases developed reacting on the nitroglycerin and thus accelerating the decomposition.

We next come to the treatment a powder undergoes during manufacture. Whether passed under steam-heated or high-pressure rolls, whether kneaded for hours in a mixing machine, squeezed from a die with an unnecessary amount of pressure and friction, due to a defect in or bad construction of the die, whether it be dried for weeks and months at temperatures far above the normal, everything tends to destroy the equilibrium of the nitrocellulose. Years ago the author showed that there is a critical point for mixtures, such as blasting gelatine or smokeless powders at or about 45° C., yet during manufacture this temperature is frequently approached and sometimes exceeded.

^a Dr. W. Will, "Untersuchungen über die Stabilität von Nitrocellulose 2. Mitteilung. Der Grenzzustand der Nitrocellulose in quantitativer Beziehung." Neubabelsberg, 1902, p. 28.

In some countries the heat test is still carried out at a temperature of 65° C., and if the explosive stands it for, say, thirty minutes, the result is considered satisfactory. Yet how often have we seen this temperature attained during manufacturing operations, and maintained for hours! Is this reasonable?

We will assume now that we have taken every precaution to manufacture an explosive which, as regards purity of its ingredients and as regards care in its preparation, leaves nothing to be desired. We were told everywhere until about ten years ago, and are still told so in this country, that the explosive must be heated to a temperature varying from 65° to 82° C. without developing sufficient nitrous acid fumes within, say, ten minutes to color potassium iodide paper. The vagaries of this test are very amusing. Eleven years ago^a the author was the first to show how it could be masked and falsified. The potassium iodide paper itself is an uncertain factor. Great precautions must be taken in its preparation, while the thickness of the paper is such a disturbing factor that the papers from one official source give a test nearly double those from another.

Various other tests on similar lines have been proposed to replace the potassium iodide test, but not one of them is a true test of stability. The potassium iodide, or the diphenylamine test, if always carried out under identical conditions, are good enough as a rough check on the manufacture. They do not, however, show whether the material itself is so constituted as to remain stable. This is, perhaps, of small importance in the case of nitroglycerin or an aromatic nitro-compound with their relatively simple structure, but it is all important for nitrocellulose, where the heat test in the opinion of most experts is of little value as a criterion of the finished article. In order to judge of stability, the critical point at which an explosive breaks down must be found, and it is also necessary to determine whether decomposition proceeds regularly or at a dangerous and increasing rate when this point is passed. A number of tests have been proposed to fulfill these conditions. They are all based on the principle that a small quantity of explosive is heated to a temperature which causes decomposition comparatively quickly yet gives sufficient time to differentiate results. In France this temperature was 110° C., but all the modern so-called "destruction" tests are made between 130° and 135° C.

All these tests require a considerable amount of time and constant supervision by a chemist. A rapid and reliable method is to heat the explosive in long glass tubes immersed in a bath of amyl alcohol provided with a reflux condenser, and to note the time that elapses

^a The Chemical Stability of Nitro-compound Explosives, "Journal of the Society of Chemical Industry," April 30, 1897.

before a distinct coloration in the tube is observed. This method compares very favorably with all others.

As I frequently mentioned, the duration of the heat test is practically halved by a rise in temperature of 5° C., and Will has confirmed this by proving that the volume of gases evolved is doubled at the same time. This is, however, only correct for temperatures above 45° C., the critical point for nitrocellulose. Below 40° C. the durability of an explosive properly prepared with it increases exceedingly rapidly, and it may be safely assumed that under 20° C. its stability is permanently assured.

This contention has been proved in practice. The author does not know of a single authenticated instance of decomposition in an explosive magazine where the temperature has been kept within the permissible limit.

This simple precaution was, however, neglected in a good many instances by both naval and military authorities. It was and still is the practice in men-of-war to arrange the ammunition stores and powder magazines in close proximity to boilers and engines, frequently without any ventilation, whilst at times explosives of all kinds are stored together. Fourteen years ago^a the author discussed this arrangement, and drew attention to the dangers arising therefrom. A dozen explosions on men-of-war and a disaster like that on the *Jena* occurred before an alarm was raised, and now all navies are hurriedly installing refrigerating apparatus. This is all very well as far as it goes if the machinery does not break down at the critical moment; but can not designers of war ships find another place for ammunition? Why go to the length of all sorts of precautions when it should not be impossible to remove the cause of deterioration altogether?

This misplacing of ammunition stores is only slightly mitigated by the fact that twenty years ago the manufacture of smokeless powders had only just begun, and nobody knew much about them. Worse than this, however, was the action of many governments in at once erecting their own powder works, without any experience in the manufacture of nitrocompounds to go upon, and relying entirely on what private manufacturers cared to show them, and on what they themselves could find out by experiments. Some of their powders made fifteen and twenty years ago are still in service, and are now the objects of suspicion.

It is, nevertheless, not fair to throw the whole of the blame on the explosive charge. How would the priming and detonating compositions used in gun charges and shells behave under unfavorable circumstances? Fulminate of mercury, potassium chlorate, sulphur, antimonypentasulphide, picric acid, and other chemicals are con-

^a Journal of the Society of Chemical Industry, 1894, p. 583.

tained in such compositions, and it is open to question whether proper tests are always carried out as regards their purity and stability under all conditions.

Fearing the lack of stability in smokeless powders, which in the early days of their manufacture was not without justification, inventors began to look around for so-called "stabilizers," that is to say, additional ingredients, which would neutralize the nitrous acid liberated on decomposition. Some people thought that if a little ether alcohol was left in the powder it would act as a stabilizer, and in order to prevent the rapid escape of the solvent on storage, a little amyl alcohol was added, thus slightly raising the boiling point of the solvent.^a As a matter of fact, this would merely constitute absorption of the nitrous vapors, but would not prevent their being given off again on heating.

A better plan is the addition of "stabilizers," which would form stable compounds with the nitrous acid; for instance, aniline, which the Nobel factory at Avigliana used in their gun cotton twenty-four years ago, and which both they and the Italian Government employ for service ballistite. Diphenylamine and, it is said, vaseline would act in a similar way. The stable compounds formed from stabilizers, like amidoazobenzol and other aromatic nitro compounds, retain the nitrous acid, and thus transform the reaction into a slow and regular one, which keeps the powder in good condition as long as there is any stabilizer left. The length of time a powder remains in good condition will therefore only depend on the proper constitution and manufacture of the powder.

Stabilizers, like diphenylamine and aniline, will also reveal their presence as soon as the powder goes wrong, since the compounds formed with them by the action of nitrous acid show as spots or stripes of peculiar colors, varying either in shade or intensity as decomposition progresses. Since the French commissioners on the *Jena* accident emphasized this fact, already known in Germany and Italy, everybody speaks of "révélateurs," the addition of an indicator, as being a panacea. As a matter of fact the author considers it only a needlessly alarming arrangement, like an alarm thermometer, and unnecessary with a good powder stored under proper conditions, but which would cause commanders of warships to nervously watch their stores after the faintest indication, without giving them any remedy in midocean. The whole idea is not new, having been patented by Nicholson and Price in 1871.^b

What we must aim at is an explosive which is durable and stable under all ordinary conditions of use, and even under some extraor-

^a Chambre des Députés, "Rapport sur les causes de la catastrophe de l'*Jena*," Paris, 1907.

^b British patent No. 2430, of September 15, 1871.

dinary ones, just as in the case of the old black powder. In the author's opinion, and his view is shared by very eminent colleagues, there can be no doubt that nitrocotton (and for the matter of that any other nitrocellulose) is not a suitable ingredient for a service powder. Having built or reconstructed a number of works and seen quite half of all those in Europe, he ventures to speak with some authority. Let us again recapitulate its defects. Made from a material which is most complex and liable to form unstable compounds, we elect to use it in a form which can neither be clean, nor of uniform growth, nor even of constant composition. The conditions of manufacture are such that in the absence of very special precautions the nitrocotton retains unstable compounds and is liable to decompose. Under the influence of heat, of certain additions or ingredients, of unsuitable treatment or friction, the nitrocotton may decompose and react in a progressive manner upon the other ingredients. It requires a solvent in order to be brought into a physical state which will permit the rate of burning of the powder to be regulated. Such solvent, if volatile, requires prolonged heating to drive it off as completely as possible. This heating helps to shorten the life of the powder, and any solvent remaining behind affects its ballistic properties. Nitrocellulose is not a uniform compound by any means, and it is almost impossible to make sure that every batch shall have the same composition and effect. The latter by no means depends on the percentage of nitrogen being the same, though this condition may be fulfilled by suitable blending. For instance, a mixture of soluble and insoluble nitrocellulose would not have the same effect as a nitrocellulose prepared direct, although each may contain the same percentage of nitrogen.

The question will naturally be asked, What will be the powder of the future? If we may venture a prophecy, the future belongs to a stable nitrocompound of the aromatic series, perhaps in conjunction with nitroglycerin. Such nitrocompounds have already been proposed, and sooner or later one will be found that meets all requirements. Although every service will be reluctant to make a change, yet having learned to appreciate the value of scientific research, some government will be sure to make a bold plunge, when all others will soon follow suit.